High Temperature Polymers for Proton Exchange Membrane Fuel Cells

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(ABSTRACT)

Novel proton exchange membranes (PEMs) were investigated that show potential for operating at higher temperatures in both direct methanol (DMFC) and H_2/air PEM fuel cells. The need for thermally stable polymers immediately suggests the possibility of heterocyclic polymers bearing appropriate ion conducting sites. Accordingly, monomers and random disulfonated poly(arylene ether) copolymers containing either naphthalimide, benzoxazole or benzimidazole moieties were synthesized via direct copolymerization. The ion exchange capacity (IEC) was varied by simply changing the ratio of disulfonated monomer to nonsulfonated monomer in the copolymerization step. Water uptake and proton conductivity of cast membranes increased with IEC. The water uptake of these heterocyclic copolymers was lower than that of comparable disulfonated poly(arylene ether) systems, which is a desirable improvement for PEMs. Membrane electrode assemblies were prepared and the initial fuel cell performance of the disulfonated polyimide and polybenzoxazole (PBO) copolymers was very promising at 80 ^{o}C compared to the state-of-the-art PEM (Nafion®); nevertheless these membranes became brittle under operating conditions. Several series of poly(arylene ether)s based on disodium-3,3'-disulfonate-4,4'-dichlorodiphenylsulfone (S-DCDPS) and a benzimidazole-containing bisphenol were synthesized and afforded copolymers with enhanced stability. Selected properties of these membranes were compared to separately prepared miscible blends of disulfonated poly(arylene ether sulfone) copolymers and polybenzimidazole (PBI). Complexation of the sulfonic acid groups with the PBI structure reduced water swelling and proton conductivity.

The enhanced proton conductivity of Nafion® membranes has been proposed to be due to the aggregation of the highly acidic side-chain sulfonic acid sites to form ion channels. A series of side-chain sulfonated poly(arylene ether sulfone) copolymers based on methoxyhydroquinone was synthesized in order to investigate this possible advantage and to couple this with the excellent hydrolytic stability of poly(arylene ether)s. The methoxy groups were deprotected to afford reactive phenolic sites and nucleophilic substitution reactions with functional aryl sulfonates were used to prepare simple aryl or highly acidic fluorinated sulfonated copolymers. The proton conductivity and water sorption of the resulting copolymers increased with the ion exchange capacity, but changing the acidity of the sulfonic acid had no apparent effect.

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6FAP	2,2'-bis(3-amino-4-hydroxyphenyl)-hexafluoropropane
6FNP	2,2'-bis(3-nitro-4-hydroxyphenyl)-hexafluoropropane
6FS-XX	disulfonated poly(arylene ether sulfone) – potassium sulfonate salt form; based on SDCDPS, DCDPS, Bisphenol AF; XX = degree of disulfonation
6FSH-XX	disulfonated poly(arylene ether sulfone) – sulfonic acid form; based on SDCDPS, DCDPS, and Bisphenol AF; XX = degree of disulfonation
AFM	atomic force microscopy
BA	benzoic acid
BAPF	9,9-bis(4-aminophenyl)fluorene
BAPFDS	bis(4-aminophenyl)fluorene-2,7-disulfonic acid
m-BAPS	bis[4-(3-aminophenoxy)phenyl] sulfone
BAPS-XX	disulfonated polyimide copolymer – based on *m*-BAPS, SA-DADPS, and NDA; XX = degree of disulfonation
BI	benzimidazole
Bisphenol-AF	4,4'-hexafluoroisopropylidene)diphenol
BDA	4,4'-diamino-2,2'-biphenyl disulfonic acid
BP	4,4'-biphenol
6FS-XX	disulfonated poly(arylene ether sulfone) – potassium sulfonate salt form; based on SDCDPS, DCDPS, and BP; XX = degree of disulfonation
BPS-BI	disulfonated poly(arylene ether sulfone benzimidazole) – potassium sulfonate salt form, based on SDCDPS, DCDPS, BP and HPBI
BPSH-BI	disulfonated poly(arylene ether sulfone benzimidazole) – sulfonic acid form, based on SDCDPS, DCDPS, BP and HPBI
BPSH-XX	disulfonated poly(arylene ether sulfone) - acid form; based on SDCDPS, DCDPS, and BP; XX = degree of disulfonation
DCDPS	4,4'-dichlorodiphenylsulfone
DFDPS	4,4'-difluorodiphenylsulfone
DMAc	N,N-dimethylacetamide
DMFC	direct methanol fuel cell
DMSO	dimethylsulfoxide
DSC	differential scanning calorimetry
EW	equivalent weight
FHQS-XX	partially fluorinated sulfonated poly(arylene ether sulfone) – XX = degree of sulfonation
FT-IR	fourier transform infrared spectroscopy
GPC	gel permeation chromatography
HPA	heteropolyacid
HPBI	5,5'-Bis[2-(4-hydroxyphenyl)benzimidazole]
HOHQS-XX	hydroxyl-containing poly(arylene ether sulfone) copolymer - XX = molar ratio of hydroxyl groups per repeat unit
HQ	hydroquinone
IEC	ion exchange capacity
IV	intrinsic viscosity

IQ	isoquinoline
MEA	membrane electrode assembly
MHQ	methoxyhydroquinone
MHQS-XX	methoxy-containing poly(arylene ether sulfone) copolymer – based on MHQ, HQ, and DCDPS, XX = molar ratio of MHQ to DCDPS
NDA	1,4,5,8-naphthalenetetracarboxylic dianhydride
NMP	N-methylpyrrolidinone
NMR	nuclear magnetic resonance
ODA	4,4'-oxydianiline
ODADS	4,4'-diaminodiphenylether-2,2'-disulfonic acid
ODA-XX	disulfonated polyimide copolymer (ODA, SA-DADPS, and NDA)
ODBA	4,4'-oxydibenzoic acid
PBI	poly(benzimidazole) - poly(5,5'-benzimidazole-2,2'-diyl-1,3-phenylene)
PBO	poly(benzoxazole)
m-PDA	*m*-phenylenediamine
PDA-XX	disulfonated polyimide copolymer (PDA, SA-DADPS, and NDA)
PEEK	poly(ether ether ketone)
PEM	proton exchange membrane
PEMFC	proton exchange membrane fuel cell
PPA	polyphosphoric acid
PSU	polysulfone
SA-DADPS	3,3'-disulfonic acid-bis[4-(3-aminophenoxy)phenyl]sulfone
S-DADPS	disulfonate-bis[4-(3-aminophenoxy) phenyl]sulfone
S-DCDPS	3,3'-disulfonate-4,4'-dichlorodiphenylsulfone
S-DFDPS	3,3'-disulfonate-4,4'-difluorodiphenylsulfone
S-DFK	sodium 5,5'-carbonylbis(2-fluorobenzenesulfonate)
SHQS-XX	sulfonated poly(arylene ether sulfone) – XX = degree of sulfonation
SODBA	disodium-2,2'-disulfonate-4,4'-dicarboxydiphenyl ether
SPI	sulfonated polyimide (BDA, ODA, and NDA)
TEA	triethylamine
TGA	thermogravimetric analysis
Udel	poly(arylene ether sulfone)
Ultem	poly(etherimide)
UV-VIS	ultraviolet-visible spectroscopy

CHAPTER 1

RESEARCH SIGNIFICANCE AND IMPACT

Proton exchange membrane (PEM) fuel cells are becoming increasingly important as alternative energy sources for stationary, automobile and portable power. This is evident by the recent presidential Hydrogen Fuel Initiative to reverse the United States' growing dependence on foreign oil by developing commercially viable clean, hydrogen-power fuel cell technology. In 2003, the United States consumed an average of 20 million barrels of oil and natural gas per day, or 7.3 billion barrels per year. U.S. oil reserves total 22.7 billion barrels, which would last less than eight years at today's rates of consumption and imports, and gasoline for cars and light trucks accounts for about 45% of U.S. oil consumption. The need for viable alternative energy conversion technology is obvious. Proton exchange membrane fuel cells generate more power for a given volume or weight of a hydrogen-air fuel cell than any other type of fuel cell. This high-power density characteristic has the potential to be compact and lightweight. In addition, the operating temperature is less than 120 ºC, which allows rapid start-up. These traits and the ability to quickly change power output are some of the characteristics that make the proton exchange membrane fuel cell the top candidate for several power applications. In addition, proton exchange membrane fuel cells have drawn a lot of attention because of their high efficiencies, quiet operation, use of fuel from totally renewable resources, and environmentally friendly processes. Ideally, the only byproduct of a hydrogen-powered PEM fuel cell is water. However, there are many challenges that face materials scientists to prepare catalysts layers and polymeric materials that can operate under the aggressive in-cell environment for long times. It is recognized in the fuel cell industry that cost is still the major issue. Reduction of cost and improved performance are two major goals of almost all companies working on this technology. Most of these organizations are working to adapt current technology, which is typically accomplished in small steps, but bold improvements are needed. One such approach is to completely replace the costly perfluorinated sulfonic acid membranes with novel polymeric systems. Heterocyclic polymers are used in many areas such as microelectronics, automotive, structural adhesives and aerospace industries due to their excellent thermal and chemical resistance and superior mechanical integrity. These properties suggested that appropriate heterocyclic aromatic polymer systems should be good candidates for proton exchange membranes.

CHAPTER 2

LITERATURE REVIEW

2.1. Fuel Cells

A fuel cell is an electrochemical device that converts chemical energy directly into electrical energy. Although there are similarities to a dry-cell battery, a fuel cell does not undergo a material change or run down.[1] In principle, it does not require recharging and operates as long as fuel is available. Sir William Grove is credited with first introducing the concept of a hydrogen/oxygen fuel cell in 1839, though the fuel cell did not become important until the 1960s when it was used by NASA in the Gemini space program.

A fuel cell produces electricity, water, and heat from fuel and oxygen. The fuel is typically hydrogen or methanol. When pure hydrogen is used, the only byproduct is water. This benign by-product makes the fuel cell an environmentally friendly energy source. The conventional way of converting fuel energy to electrical energy is by some form of heat engine (steam or internal combustion). In practice, the most efficient heat engines are limited to a maximum theoretical efficiency of about 40-50%. In contrast, the fuel cell is not a heat engine; it converts energy isothermally. It is not subject to the Carnot Cycle, and almost all the chemical energy of the fuel may be converted to electricity. Additionally, fuel pumps and if necessary, electrolyte pumps are the only moving parts, so this means quiet operation, high reliability, and freedom from maintenance.

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[1] Winter, M.; Brodd, R.J. What Are Batteries, Fuel Cells, and Supercapacitors? *Chem. Rev.* **2004**, *104*, 4245-4270.

A separator or electrolyte, which allows for a flow of ionic charges but prevents the transfer of chemical species, is needed in electrochemical cells like fuel cells and batteries. The type of conductive electrolyte used is what characterizes a fuel cell. The major types of fuel cells, along with the type of electrolyte, are summarized in Table 2-1.

Table 2-1. Types of fuel cells[2]

Type of Fuel Cell	Electrolyte	Operating Temperature	Efficiency	Electric Power	Possible Applications
Alkaline (AFC)	Potassium Hydroxide	60-90 ^oC	45-60%	Up to 20 kW	Submarines, Spacecraft
Molten Carbonate (MCFC)	Immobilized Liquid Molten Carbonate	650 ^oC	45-60%	> 1 MW	Power Stations
Solid Oxide (SOFC)	Ceramic	1000 ^oC	50-65%	> 200 kW	Power Stations
Phosphoric Acid (PAFC)	Immobilized Liquid Phosphoric Acid	200 ^oC	35-40%	> 50 kW	Power Stations
Proton Exchange Membrane (PEMFC)	Ion Exchange Membrane	60-130 ^oC	40-60%	Up to 250 kW	Vehicles, Stationary
Direct Methanol (DMFC)	Ion Exchange Membrane	60-130 ^oC	40%	< 10 kW	Portable Applications

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[2] Fuel Cell Today, Johnson Matthey Public Limited Company. www.fuelcelltoday.com (accessed Jan 2005).

2.1.1. Proton Exchange Membrane Fuel Cell (PEMFC)

To date, the proton exchange membrane, or polymer electrolyte membrane, fuel cell (PEMFC) is the most promising candidate of all fuel cell systems in terms of mode of operation and applications. PEMFCs currently operate at relatively low temperature (30 – 150 ^oC) but generate a specific power and power density higher than any other type of fuel cell. The operation of a hydrogen-oxygen proton exchange membrane (PEM) fuel cell is relatively straightforward. The “heart” of the PEMFC is the membrane electrode assembly (MEA) (or catalyst-coated membrane, CCM) which consists of two electrodes (anode, cathode) separated by an ion-conducting polymer electrolyte (Figure 2-1). When supplied with fuel (hydrogen) and oxidant (oxygen), two electrochemical half-cell reactions take place.

Equation 1-1 **Anode:** $H_2 \rightarrow 2H^+ + 2e^-$

Equation 1-2 **Cathode :** $\frac{1}{2} O_2 + 2H^+ + 2e^- \rightarrow H_2O$

Hydrogen fed to the anode is oxidized to produce protons and electrons in the presence of a catalyst. The resulting protons are transported in an aqueous environment across the electrolyte to the cathode. Useful electrical energy is harnessed by electrons moving through an external circuit before allowing them to reach the cathode. At the cathode, gaseous oxygen from the air is reduced and combined with the protons and electrons. The overall cell reaction yields one mole of water per mole of hydrogen and half mole of oxygen.

Equation 1-3 **Overall:** $H_2 + \frac{1}{2} O_2 \rightarrow H_2O$

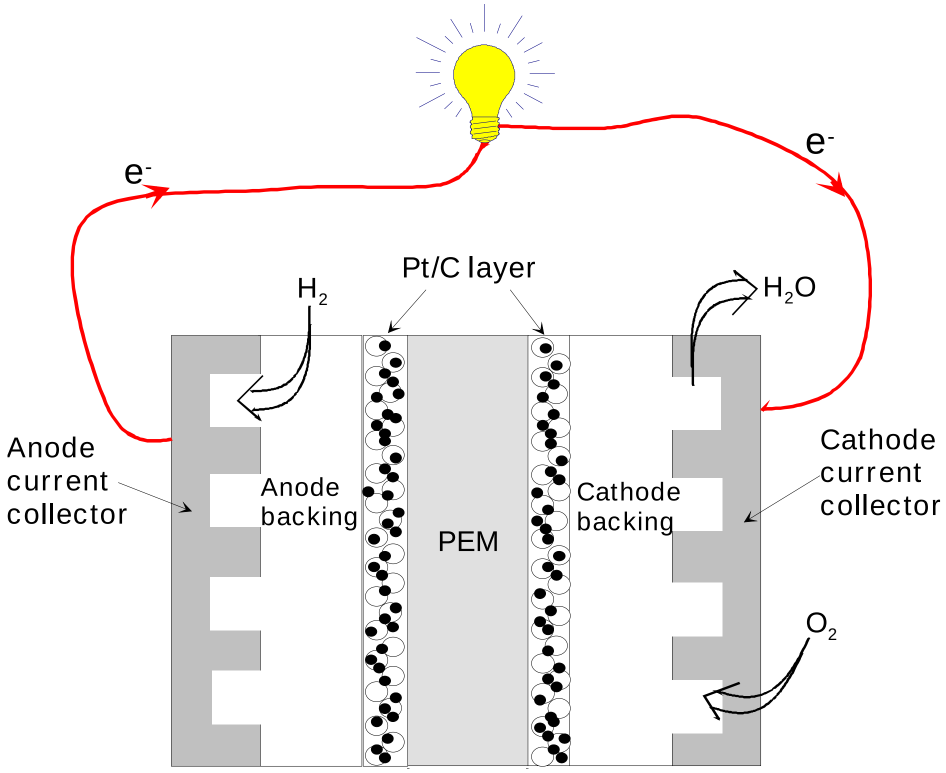

Figure 2-1. Schematic of a proton exchange membrane fuel cell[1]

PEMFCs use a proton-conducting polymer membrane as an electrolyte, which is typically a poor proton conductor unless water is present. Therefore the hydration of a PEM is very important to the performance of the fuel cell. The water sorption of sulfonated polymers has a profound effect on membrane conductivity and mechanical properties.[3] Membranes with little water uptake typically have low proton conductivity, while the mechanical strength is compromised in membranes with high water sorption.[4] The water content in ionomers is represented by both the water uptake and the number of

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[3] Kopitzke, R.W.; Linkous, C.A.; Anderson, H.R.; Nelson, G.L. Conductivity and Water Uptake of Aromatic-Based Proton Exchange Membrane Electrolytes, *J. Electrochem. Soc.* **2000**, *147*, 1677-1681.

[4] Gao, Y.; Robertson, G.P.; Guiver, M.D.; Jian, X. Synthesis and Characterization of Sulfonated Poly(phthalazinone ether ketone) for Proton Exchange Membrane Materials. *J. Polym. Sci.: Part A: Polym. Chem.* **2003**, *41*, 497-507.

water molecules per SO_3^- (λ). The water uptake is calculated by weighing the membrane under hydrated and dry conditions (Equation 1-4), and λ can be calculated from the water uptake and the ion-exchange capacity (Equation 1-5).

Equation 1-4 $$\textbf{Water Uptake (\%)} = [(w_{wet} - w_{dry}) / w_{dry}] * 100$$

Equation 1-5 $$\lambda = 1000 * [(w_{wet} - w_{dry}) / w_{dry}] / (18 * \text{IEC})$$

The ion-exchange capacity, or IEC, is usually defined as the moles of fixed SO_3^- sites per gram of polymer. The IEC of membranes can be experimentally determined by potentiometric titration of the acid groups with base and calculated by Equations 1-6 and 1-7. Another common term for the IEC is the equivalent weight (EW), which is the inverse of the IEC.

Equation 1-6 $$\text{Mass}_{total} = F_1 M_1 + F_2 M_2$$

M_1 = molecular weight of the nonsulfonated repeat unit
M_2 = molecular weight of the sulfonated repeat unit
F_1 and F_2 are the respective molar ratio based on the charged monomers

Equation 1-7 $$\text{IEC} = \text{Degree of Sulfonation} * 2 * 1000 / \text{Mass}_{total}$$

In PEM fuel cells the proton conductivity of the membrane is particularly important since it plays a significant role in the performance of the fuel cell. Higher levels of proton conductivity allow higher power densities to be achieved. The proton conductivity of hydrated polymer electrolytes dramatically increases with temperature and water content; therefore, it is of importance to report the exact conditions under which the proton conductivity is measured. Currently, automotive companies are pushing for high temperature operation (100 ^{o}C) at 25% relative humidity, but will likely accept good conductivity at 50% relative humidity. The proton conductivity of membranes can be measured by AC impedance spectroscopy. Under true fuel cell conditions, the protons move through the plane of the membrane. However, through-plane conductivity experiments are difficult to perform due to significant interfacial resistances that occur in testing. Conversely, a facile method was designed at Los Alamos National Laboratories to determine membrane conductivities by measuring the resistance in the plane of the membrane.[5] This technique allows for more measurable resistances and a simplified set-up. The proton conductivity, σ, is calculated from the impedance data using Equation 1-8. The minimum resistance is derived from the low intersect of the high frequency semicircle on a complex impedance plane with the Re(z) axis.

Equation 1-8 $\sigma = \rho^{-1} = L / (R*W*T)$

ρ^{-1} = resistivity
L = length between electrodes
W = width of sample
T = thickness of sample
R = minimum resistance

Although there are many other properties of PEMs that are important correlations to fuel cell performance (thermal stability, methanol crossover, electroosmotic drag, etc.),

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[5] Zawodzinski, T.A.; Neeman, M.; Sillerud, L.O.; Gottesfeld, S. Determination of Water Diffusion Coefficients in Perfluorosulfonate Ionomeric Membranes. *J. Phys. Chem.* **1991**, *95*, 6040-6044.

the IEC, water uptake and proton conductivity are essential to evaluate membranes as candidates for PEM fuel cells.

Proton exchange membranes for PEMFCs have to meet the following requirements:

- Low cost
- Good film-formation
- High proton conductivity (especially at low relative humidity)
- Low electronic conductivity
- Water retention above 100 °C
- Thermal, oxidative and hydrolytic stability
- Effective reactant separator
- Capable of fabrication into MEAs
- Mechanical durability at high temperature (80 – 140 °C) for long times
    - 2,000 hours for portable power
    - 5,000 – 10,000 hours for automobiles
    - 40,000 hours for stationary applications

Another challenge is to produce inexpensive materials that meet the above requirements. Presently, some of the most promising candidates for proton-exchange membranes are high performance polymers, ie. polyimides, poly(ether ketone)s, poly(arylene ether sulfone)s, polybenzimidazoles, etc. Advantages of using these materials are: lower cost than perfluorinated membranes, inclusion of polar groups to improve water uptake over a range of temperatures, and the possibility of recycling by conventional methods.

2.1.2. Commercially Available Proton Exchange Membranes

NASA employed a PEMFC on the Gemini program as an auxiliary power source, which initially used crosslinked sulfonated polystyrene as the membrane. This copolymer possessed insufficient oxidative stability under operating conditions. A major breakthrough in PEMFC technology came with the advent of perfluorosulfonic acid Nafion® membranes. These membranes provided improved chemical stability and an increase in conductivity compared to the sulfonated polystyrene membranes. The performance and lifetime of PEMFCs have significantly improved since the introduction of Nafion® in 1966 by DuPont. Nafion® is the most widely studied PEM because it possesses high proton conductivity, good mechanical strength, excellent stability, and is commercially available.[6] The high electronegativity of the fluorine atoms bonded to the same carbon atom as the sulfonic acid group makes the -SO_3H a superacid. The Teflon-like backbone (~87% in Nafion 1100) provides Nafion with excellent oxidative stability at the cathode and also at the anode, which may generate small amounts of hydrogen peroxide. The most dramatic result obtained using Nafion® was that the lifetime of the PEMFCs increased by at least four orders of magnitude over previous membranes. It has been reported that a lifetime of over 50,000 hours has been achieved at 80 ^{o}C.[7] One of the major drawbacks of perfluorosulfonic acid membranes has been and still is their high cost (~\$700/m^2 for films). This high cost is due to the expensive fluorinated comonomer. Nafion® is synthesized is in four steps: (1) the reaction of tetrafluoroethylene with SO_3 to form the cyclic sulfone, (2) the condensation of these products with sodium carbonate

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[6] Mauritz, K.A.; Moore, R.B. State of Understanding of Nafion. *Chem. Rev.* **2004**, *104*, 4535-4586.

[7] Rikukawa, M.; Sanui, K. Proton-Conducting Polymer Electrolyte Membranes Based on Hydrocarbon Polymers. *Prog. Polym. Sci.* **2000**, *25*, 1463-1502.

followed by copolymerization of the perfluoro vinyl ether sulfonyl fluoride with the tetrafluoroethylene to form an insoluble but thermoplastic resin, (3) the basic hydrolysis of this sulfonyl fluoride extruded film to form a perfluorosulfonic polymer and (4) the chemical exchange of the sodium counterion with a proton in an appropriate electrolyte.[8] The general formula for Nafion® is shown in Figure 2-2.

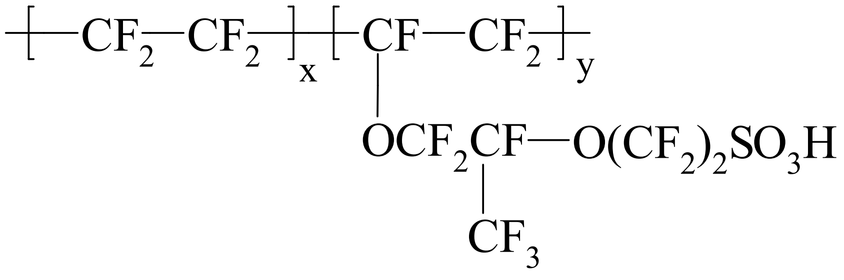

Figure 2-2. Structure of the Nafion® membrane: x = 6-10, y = 1

The values of x and y (above) represent compositions that can be changed to alter the EW of Nafion®. For example, DuPont nomenclature for Nafion 117® is that the membrane is 1100 EW (0.91 meq/g ion exchange capacity) and 7 mil thick (1 mil = 25.4 microns).

Improvements in the membrane structure and conductivity were achieved by producing composite membranes.[9] W.L. Gore and Asahi Chemicals successfully reinforced perfluorosulfonic acid membranes with Teflon fabric. Thinner films could then be prepared that had improved conductivity and mechanical properties, but also

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[8] Savadago, O. Emerging Membranes for Electrochemical Systems: (I) Solid Polymer Electrolyte Membranes for Fuel Cell Systems. *J. New Mat. Electrochem. Systems* **1998**, *1*, 47-66.

[9] Heitner-Wirguin, C. Recent Advances in Perfluorinated Ionomer Membranes: Structure, Properties and Applications. *J. Membr. Sci.* **1996**, *120*, 1-33.

increased fuel and oxidant permeability. Additionally, composites were made by swelling the perfluorinated ionomeric membrane with an ionic liquid to improve its high temperature stability.[10] By running the PEMFC at higher temperature, the oxygen reduction kinetics and carbon monoxide poisoning problems are improved.

2.1.3. Sulfonated Polyimides

2.1.3.1. General Considerations

Five-membered ring polyimides are high performance thermally stable materials that have been investigated for many years.[11] However, when sulfonated five membered ring (phthalic) polyimides are used for proton exchange membranes in fuel cells, they quickly degrade and become brittle, whereas six-membered ring (naphthalenic) polyimides do not. It is likely that hydrolysis of the phthalimide structure under strong acid conditions quickly leads to chain scission and causes the membrane to become brittle.[13] Since the six-membered ring of the naphthalenic polyimide is much more stable to hydrolysis, this membrane is better suited for fuel cell applications.[12] It was reported that a sulfonated six-membered ring polyimide was stable for over 3000 hours at 60 °C and that it performed as well as Nafion 117® under fuel cell conditions.[8]

Genies *et al.* used model compounds along with IR and NMR to examine the nature of hydrolysis associated with the sulfonic acid group (needed for proton

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[10] Doyle, M.; Choi, S.K.; Proulx, G. High-Temperature Proton Conducting Membranes Based on Perfluorinated Ionomer Membrane-Ionic Liquid Composites. *J. Electrochem. Soc.* **2000**, *147*, 34-37.

[11] Feger, C.; McGrath, J.E.; Khojasteh, M.M. *Polyimides: Materials, Chemistry and Characterization.* Elsevier: New York, 1988.

[12] Rusanov, A.L. Novel Bis(Naphthalic Anhydrides) and Their Polyheteroarylenes with Improved Processability. *Adv. Polym. Sci.* **1994**, *111*, 115-175.

conduction) in phthalic and naphthalenic polyimides.[13] Model compounds of the sulfonic acid containing phthalic imide (Model A) and the sulfonic acid containing naphthalenic imide (Model B) were prepared by a one-step high temperature condensation in *m*-cresol. NMR spectroscopy showed that after aging Model A in distilled water at 80 ^{o}C for 1 hour the structure was modified. After aging for 10 hours, ^{13}C NMR demonstrated that the carbon peaks associated with the starting compound disappeared. In addition, ^{13}C NMR was used to quantitatively determine the amount of imide, amic acid, and diacid as a function of time during the aging process of Model A. From zero to two hours of aging, the amic acid is formed preferentially to the diacid. This result was interesting because the amic acid should easily hydrolyze to the diacid in water.

In comparison, no structural modification of Model B was observed before 120 hours of aging in water at 80 ^{o}C. However, after 120 hours two small doublets appeared in the ^{1}H NMR and several additional peaks became noticeable in the ^{13}C NMR. It was determined by NMR and IR spectroscopy that the hydrolysis products were an imide/carboxylic acid and an imide/anhydride. Model B was then aged for 1200 hours at 80 ^{o}C to quantitatively determine the amount of hydrolysis products as a function of time. The relative intensity of the peaks due to carboxylic acid was constant after some time. The authors suggested that an equilibrium occurred between model B and the products formed during hydrolysis, and therefore the conversion to hydrolysis products was limited to about 12%.

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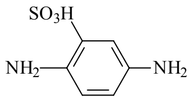
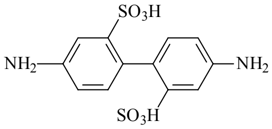
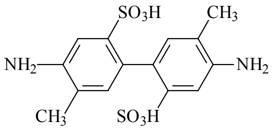
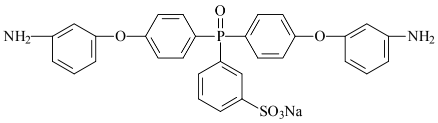
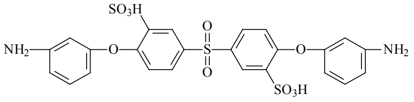
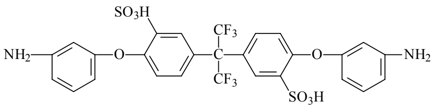
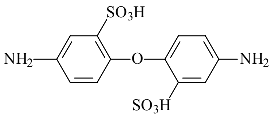
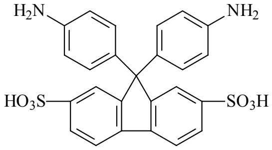
[13] Genies, C.; Mercier, R.; Sillion, B.; Petiaud, R.; Cornet, N.; Gebel, G.; Pineri, M. Stability Study of Sulfonated Phthalic and Naphthalenic Polyimide Structures in Aqueous Medium. *Polymer* **2001**, *42*, 5097-5105.

To date, the synthesis of sulfonated six-membered ring polyimide copolymers has been by a direct copolymerization procedure. This approach requires that a sulfonated monomer is used in the copolymerization, as opposed to sulfonation of the parent polymer. Stoichiometric amounts of sulfonated diamine relative to nonsulfonated diamine, and NDA as the dianhydride, have been used for sulfonated copolyimide synthesis. A 1:1 stiochiometric ratio of total diamine to dianhydride was used to obtain high molecular weight polymer. The degree of sulfonation could be varied by changing the ratio of sulfonated to nonsulfonated diamine. The copolymerizations were always a one-step high temperature polycondensation in *m*-cresol; however, the catalysts employed have been varied. In all cases, the triethylammonium salt form of the sulfonated diamine is used to synthesize high molecular weight polyimides. The acid and sodium sulfonate forms of most diamines are insoluble in *m*-cresol. By adding triethylamine to a sulfonated diamine in *m*-cresol at room temperature for about 4 hours, the triethylammonium salt form of the sulfonated diamine was formed which was soluble in the reaction media. Also, the free uncomplexed aromatic amine will be more reactive. Benzoic acid and isoquinoline are used as catalysts for imide formation. The reasons for using these catalysts will be discussed further in a subsequent section. Mercier *et al.* did not use isoquinoline in their reactions, yet FT-IR of their products showed characteristic imide adsorption bands. This observation suggests that isoquinoline may not be necessary due to the use of another base, triethylamine, in the first step of the reaction.

Several sulfonated diamines which have been used for sulfonated copolymer synthesis for PEMs are shown in Table 2-2. The first three, 2,5-diaminobenzenesulfonic acid (DAB), 4,4’-diamino-2,2’-biphenyl disulfonic acid (BDA), and 4,4’-diamino-5,5’-

dimethyl-2,2’-biphenyl disulfonic acid (6TS) are commercially available, while the rest were synthesized by the investigators.

Table 2-2. Sulfonated diamines

Structure	Name	Abbreviation	Ref.
	2,5-Diaminobenzene-sulfonic acid	DAB	14
	4,4’-Diamino-2,2’-biphenyl disulfonic acid	BDA	18
	4,4’-Diamino-5,5’-dimethyl-2,2’-biphenyl disulfonic acid	6TS	24
	3-Sulfo-4’,4’’-bis(3-aminophenoxy)triphenyl phosphine oxide sodium salt	SBAPPO	17
	3,3'-Disulfonate-bis[4-(3-aminophenoxy) phenyl]sulfone	SA-DADPS	Chapter 3
	2,2-Bis[4-(4-aminophenoxy)phenyl] hexafluoropropane disulfonic acid	BAHFDS	25
	4,4’-Diaminodiphenylether-2,2’-disulfonic acid	ODADS	15
	9,9’-Bis(4-aminophenyl)fluorine-2,7-disulfonic acid	BAPFDS	26

Two of the diamines shown in Table 2-2, DAB and 3-sulfo-4',4''-bis(3-aminophenoxy)triphenyl phosphine oxide sodium salt (SBAPPO), have only one sulfonic acid group. DAB was used to prepare sulfonated five-membered ring polyimides.[14] These polymers generally have poor solubility and poor mechanical properties, so this sulfonated diamine is rarely used.[15] To improve the water retention properties and interactions with inorganic hydrates, phosphine oxide groups were introduced into sulfonated polymer systems. Shobha *et al.* described the sulfonation of 4,4'-difluoro-triphenylphosphine oxide (BFPPO) to SBFPPO.[16] The sulfonated diamine, SBAPPO, was synthesized through a nucleophilic substitution reaction of *m*-aminophenol and SBFPPO.[17] Although the monomer could be used to polymerize high molecular weight polyimides, it only bears one sulfonic acid group per repeat unit, so the resulting conductivity was lower than polyimides prepared from disufonic acid diamines.

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[14] Gunduz, N. Synthesis and Characterization of Sulfonated Polyimides as Proton Exchange Membranes for Fuel Cells. Ph.D. Dissertation, Virginia Tech, Blacksburg, VA, 2001.

[15] Fang, J.; Guo, X.; Harada, S.; Watari, T.; Tanaka, K.; Kita, H.; Okamoto, K,-I. Novel Sulfonated Polyimides as Polyelectrolytes for Fuel Cell Application. 1. Synthesis, Proton Conductivity, and Water Stability of Polyimides from 4,4'-Diaminodiphenyl Ether-2,2'-disulfonic Acid. *Macromolecules* **2002**, *35 (24)*, 9022-9028.

[16] Shobha, H.K.; Smalley, G.R.; Sankarapandian, M.; McGrath, J.E. Synthesis and Characterization of Sulfonated Poly(arylene ether)s Based on Functionalized Triphenyl Phosphine Oxide for Proton Exchange Membranes. *ACS Div. Polym. Chem., Polym. Preprs.* **2000**, *41(1)*, 180.

[17] Shobha, H.K.; Sankarapandian, M.; Glass, T.E.; McGrath, J.E. Sulfonated Aromatic Diamines as Precursors for Polyimides for Proton Exchange Membranes. *ACS Div. Polym. Chem., Polym. Preprs.* **2000**, *41(2)*, 1298-1299.

2.1.3.2. Sulfonated Polyimides Based on 4,4’-Diamino-biphenyl-2,2’-disulfonic acid (BDA)

BDA is an available disulfonated diamine that has two sulfonic acid groups attached, so it is a logical choice for polyimide synthesis for PEMs. In addition, it is the most studied sulfonated diamine used to prepare polyimides for fuel cell applications. Several groups have made copolymers using this diamine.[14,18,21]

Mercier *et al.* designed a synthetic method to produce random and block (segmented) sulfonated copolyimides. The synthetic procedure is shown in Figure 2-3 for their most studied copolymer, SPI. The first step involves preparation of short sequences of BDA condensed with NDA. An adjusted ratio of these two monomers allows one to create different block lengths of the sulfonated sequence. In the second step, the degree of sulfonation can be precisely controlled by regulating the molar ratio of BDA and the nonsulfonated diamine, which was 4,4’-oxydianiline (ODA) in SPI. It is well known that controlling the degree of sulfonation is very important because a high degree of sulfonation generally leads to high swelling or even dissolution of the polyimide membrane. If a statistically random copolymer is needed, all the monomers can be added at the beginning of the reaction. It was found that a block length of three sulfonated repeat units yields the highest conductivity.[18]

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[18] Cornet, N.; Diat, O.; Gebel, G.; Jousse, F.; Marsacq, D.; Mercier, R.; Pineri, M. Sulfonated Polyimide Membranes: A New Type of Ion-Conducting Membrane for Electrochemical Applications. *J. New Mat. Electrochem. Systems* **2000**, *3*, 33-42.

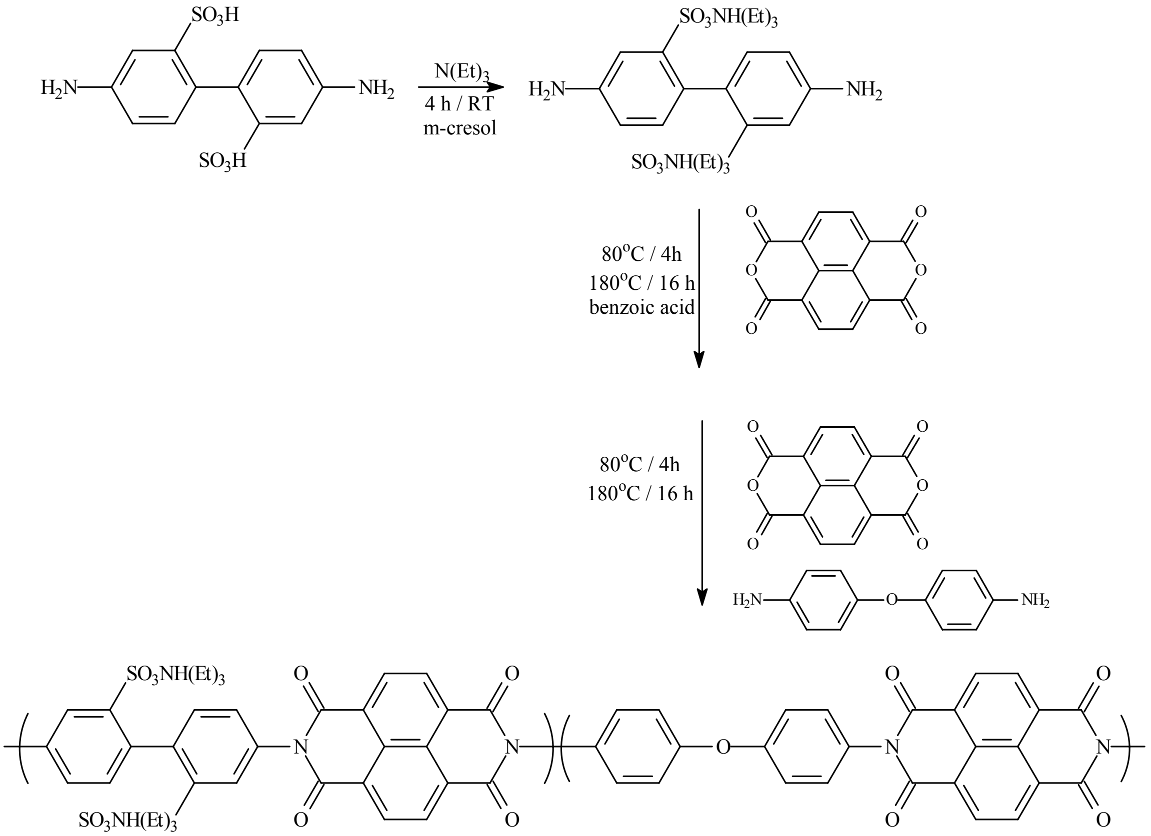

Figure 2-3. Synthesis of SPI, a sulfonated six-membered ring polyimide based on BDA, ODA, and NDA

Preliminary investigations showed that six-membered ring polyimides are promising as proton exchange membranes (PEMs); however, their poor solubility limits their use in fuel cells.[8] For example, the SPI membrane shown above is only soluble in chlorophenol. By introducing a slightly different nonsulfonated diamine, 2,2'-diamino-3,4'-biphenyl ether, the resulting polymer becomes soluble in *m*-cresol.[19] Novel sulfonated naphthalenic polyimides were prepared using BDA as the sulfonated diamine, NDA as the dianhydride and several novel nonsulfonated diamines containing ether linkages and/or bulky substituents to improve solubility.[20] The preparation of sulfonated polyimides with different ion-exchange capacities and sulfonated block lengths was also considered. The solubility of the polyimides was greatly improved by introducing phenyl-ether bonds and bulky groups into the polymer backbones. Seven diamines were prepared; however, only three were successfully polymerized. The four diamines that could not be polymerized were too rigid and precipitated during the reaction. Additionally, as has been previously shown for nonsulfonated polyimides, polymers from *meta*-amino substituted diamines had better solubility than those from *para*-amino substituted diamines. Random sulfonated copolyimides exhibited better solubility than the sequenced ones in organic solvents. Therefore, improved solubility is a result of the nonsulfonated diamine and the microstructure of the copolymer chain. For a given copolymer structure, the water uptake increased as ionic content increased. However, the number of water molecules per ionic group remained constant, which suggested that

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[19] Vallejo, E.; Pourcelly, G.; Gavach, C.; Mercier, R.; Pineri, M. Sulfonated Polyimides as Proton Conductor Exchange Membranes. Physicochemical Properties and Separation H+/Mz+ by Electrodialysis Comparison with a Perfluorosulfonic Membrane. *J. Membr. Sci.* **1999**, *160*, 127-137.

[20] Genies, C.; Mercier, R.; Sillion, B.; Cornet, N.; Gebel, G.; Pineri, M. Soluble Sulfonated Naphthalenic Polyimides as Materials for Proton Exchange Membranes. *Polymer* **2001**, *42*, 359-373.

water was mainly located in the hydrophilic domains. Both the number of water molecules per ionic group and conductivity were systematically lower for statistical copolymers than for the block copolyimides.

By introducing bulky nonsulfonated diamines into the polymer backbone, greater interchain spacings were reportedly achieved.[21,22] It was proposed, but not demonstrated, that the increased spacing could improve conductivity at low relative humidity. Incorporating the larger comonomers could prevent regular close parallel packing of the backbones and result in a more open structure, as shown by x-ray diffraction patterns. With greater interchain spacings, more free volume is available for water to occupy. This scenario leads to higher water uptake values and therefore higher conductivity, especially at low humidity.

Several research groups have investigated the same series of sulfonated copolyimides using 4,4'-(9-fluorenylidene dianiline) (BAPF) as the nonsulfonated diamine.[,23,24] By introducing the bulky diamine BAPF, the copolymers may have large free volumes. The Litt group only used 2.5 – 10 mole % of BDA, whereas McGrath's group incorporated anywhere from 20 – 80%. Okamoto *et al.* only reported copolymers with very high degrees of sulfonation (>80%). Similar methods were used to measure

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[21] Zhang, Y.; Litt, M.; Savinell, R.F.; Wainright, J.S. Molecular Design Considerations in the Synthesis of High Conductivity PEMs for Fuel Cells. *ACS Div. Polym. Chem., Polym. Preprs* **1999**, *40(2)*,. 480-481.

[22] Zhang, Y.; Litt, M.; Savinell, R.F.; Wainright, J.S.; Vendramint, J. Molecular Design of Polyimides Toward High Proton Conducting Materials. *ACS Div. Polym. Chem., Polym. Preprs.* **2000**, *41(2)*, 1561-1562.

[23] Gunduz, N.; McGrath, J.E. Wholly Aromatic Five- and Six-Membered Ring Polyimides Containing Pendant Sulfonic Acid Functional Groups. *ACS Div. Polym. Chem., Polym. Preprs.* **2000**, *41(2)*, 1565-1566.

[24] Watari, T.; Fang, J.; Tanaka, K.; Kita, H.; Okamoto, K. Ionic Conductivity and Vapor Permeation Properties of Polyimides Containing Sulfonic Acid Groups. *ACS Polym. Mat.: Sci. & Eng. (PMSE)* **2001**, *85*, 334.

conductivity, yet surprisingly the polymers prepared by Litt *et al.* showed higher conductivities at lower degrees of sulfonation. However, this work has not yet appeared in a refereed journal. Additionally, Okamoto's team synthesized sulfonated polyimides from 6TS, BAPF, and NDA; however, no significant changes in the membrane properties by changing the sulfonated diamine were reported.

2.1.3.3. Novel Sulfonated Diamines

Several novel sulfonated diamines have been synthesized to study the structure-property relationships in sulfonated polyimides. Gunduz showed the synthesis of 3,3'-Disulfonate-bis[4-(3-aminophenoxy) phenyl]sulfone (S-DADPS) and subsequent sulfonated phthalic polyimides from this monomer was possible.[14] Recently three novel sulfonated diamines, 4,4'-diaminodiphenylether-2,2'-disulfonic acid (ODADS), 9,9'-Bis(4-aminophenyl)fluorene-2,7-disulfonic acid (BAPFDS), and 2,2-bis[4-(4-aminophenoxy)phenyl] hexafluoropropane disulfonic acid (BAHFDS), have been prepared.[25] The synthesis of two of the sulfonated diamines, ODADS and BAPFDS, and the copolymers from these diamines were reported.,[26] ODADS and BAPFDS were sulfonated in fuming sulfuric acid (60% SO_3) for two hours at 60 °C. Compared to other sulfonated monomers that have been synthesized, these monomers do not "salt out" in sodium chloride. Instead, the solution of sulfuric acid and monomer are added to ice water, neutralized, and acidified. Sulfonated diamines with sulfonic acid groups attached

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[25] Zhou, W.; Watari, T.; Kita, H.; Okamoto, K,-I. Gas Permeation Properties of Flexible Pyrolytic Membranes from Sulfonated Polyimides. *Chem. Lett.* **2002**, 534-535.

[26] Guo, X.; Fang, J.; Watari, T.; Tanaka, K.; Kita, H.; Okamoto, K,-I. Novel Sulfonated Polyimides as Polyelectrolytes for Fuel Cell Application. 2. Synthesis and Proton Conductivity of Polyimides from 9,9-Bis(4-aminophenyl)fluorine-2,7-disulfonic acid. *Macromolecules* **2002**, *35(17)*, 6707-6713.

are usually insoluble in water, so Okamoto's group took advantage of this fact. Once in the acid form, the sulfonated monomer precipitated from solution, was filtered and washed with methanol. No recrystallization step to purify the monomers is discussed before polymerization for either diamine. Since the protonated amine group of ODA is a strong electron-withdrawing group, the sulfonation reaction mainly occurs at the position *meta* to the amine. The ether bond *para* to the amine group also supports the *meta*-position substitution. As for BAPFDS, since the sulfonic acid groups are on pendent rings of the polymer chain, it was suggested that polymers synthesized from this monomer would have improved stability in water (Figure 2-4). This hypothesis will be discussed further in the *Hydrolytic Stability* section.

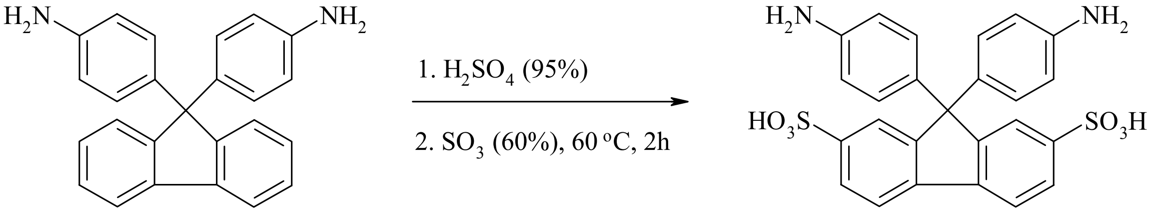

Figure 2-4. Sulfonation of 9,9-bis(4-aminophenyl)fluorene (BAPF) to BAPFDS[26]

2.1.3.4. Membrane Preparation

It is difficult to compare the sulfonated six-membered ring polyimide systems to each other because each group prepares membranes in their own way. Films of SPI polyimides and others made by Mercier *et al.* were cast directly from the reaction solution.[20] The membranes were dried under a heat lamp at 60 °C for several days to evaporate the solvent. At this point the membranes still have some resdidual *m*-cresol, so they were boiled in methanol for two hours. This process eliminates any remaining *m*-

cresol and catalysts; however, it creates pores in the membrane. The porosity is dependent upon the degree of sulfonation and ionic block length.[27] Okamoto's and McGrath's groups isolate the polymers first by precipitating them in an appropriate solvent.[28] Then the copolymer was extracted with methanol to remove any remaining catalysts and *m*-cresol. Finally, the copolymer was redissolved in DMAc, NMP, or *m*-cresol, depending on its solubility, to cast a film. Copolymers prepared from SA-DADPS have been soluble in DMAc, except at very low sulfonation levels, in which the polyimides easily dissolve in NMP. Polyimides derived from ODADS as the sulfonated diamine are soluble in *m*-cresol, but insoluble in common dipolar aprotic solvents such as NMP and DMAc, even at 50% disulfonation. By both membrane preparation methods, the water uptake is directly dependent on the degree of sulfonation. However, the water uptake for the SPI membrane was almost constant at different temperatures, due to the porosity.

2.1.3.5. Membrane Properties

Several methods have been used to determine the degree of sulfonation in the sulfonated polyimide membranes. Non-aqueous potentiometric titration, infrared spectroscopy (IR) and thermogravimetry (TGA) confirm the introduction of sulfonic acid sites. A loss in weight at around 100 °C was attributed to the absorbed water in the membrane, and a loss at about 200 °C was due to desulfonation of the polyimide film.

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[27] Cornet, N.; Beaudoing, G.; Gebel, G. Influence of the Structure of Sulfonated Polyimide Membranes on Transport Properties. *Sep. Purif. Technol.* **2001**, *22-23*, 681-687.

[28] Hong, Y.T.; Einsla, B.; Kim, Y.S.; McGrath, J.E. Synthesis and Characterization of Sulfonated Polyimides Based on Six-Membered Ring as Proton Exchange Membranes. *ACS Div. Polym. Chem., Polym. Preprs.* **2002**, *43(1)*, 666-667.

This evidence was further supported by the evolution of sulfur monoxide and sulfur dioxide. The successful introduction of sulfonate groups can be confirmed by FT-IR spectroscopy. Strong characteristic absorption peaks around 1030 and 1090 cm^{-1} were assigned to symmetric and asymmetric stretching of the sulfonic acid sites. Titration is a good method to quantitatively determine the number of sulfonic acid sites on the polymer backbone. This number is generally stated as the ion-exchange capacity (IEC), which is the milliequivalents of sulfonic acid per gram of polymer, and is essentially the reciprocal of the equivalent weight.

The conductivity of all the six-membered ring polyimides shown above was measured by impedance spectroscopy. Membranes from BDA, ODADS, and BAPFDS display increased proton conductivities with increasing temperature. High IEC values are needed (around 50% sulfonation) for the sulfonated polyimides to obtain proton conductivities near that of Nafion 117 (0.1 S/cm at 30 ^{o}C in liquid water). Additionally, the IEC of the membranes greatly influenced the conductivity. Membranes with similar IEC values had very similar conductivities, even when the sulfonated diamine was different.

2.1.3.6. Hydrolytic Stability

A topic of particular interest is the water resistance of polyimide films under working conditions of a fuel cell. A random copolymer of BDA and ODA (IEC = 2 meq/g) became brittle in water at 80 ^{o}C after 5 hours. By simply changing to a nonsulfonated diamine with flexible ether linkages, the stability improved to 200 hours at 80 ^{o}C. Okamoto *et al.* also suggest that the flexibility and basicity of the nonsulfonated diamine play a large role in water stability. Litt's group found that bulky comonomers and sequenced copolymers impart improved water resistance without sacrificing conductivity. In fact, the sequenced polyimides should also have higher conductivities. Litt *et al.* only states the hydrolytic stability of one sample with a very low IEC of 0.13 meq/g. That random copolyimide (Figure 2-5) becomes brittle after three weeks in water above 90 °C.

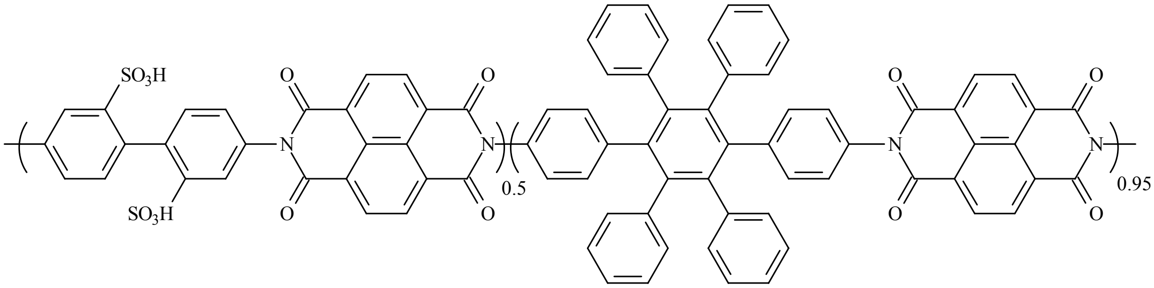

Figure 2-5. Six-membered ring copolyimide prepared with a bulky nonsulfonated diamine[21]

A comparison of the hydrolytic stability of several sulfonated six-membered ring polyimides is given in one publication. Membranes were soaked in distilled water at 80 °C until the mechanical properties degraded. When the membranes became brittle enough to break upon being lightly bent, this time was recorded. Improvements in membrane stability are shown for polymers with lower degrees of sulfonation (lower IEC) and for random copolymers, compared to block or sequenced copolymers. Additionally, the flexibility of the sulfonated diamine in the copolymer structure plays an important role in the stability. By simply changing the sulfonated diamine from the rigid BDA to the more flexible ODADS, the stability in water greatly improved. On the other hand, BAPFDS is a rigid and bulky sulfonated diamine, and it shows similar stability to the ODADS series at comparable ion-exchange capacities. It was suggested that polyimides derived from BAPFDS showed higher stability due to the highly basic sulfonated diamine. Aromatic diamines with higher basicity are generally more reactive with dianhydrides than those with lower basicity. Since hydrolysis is the reverse reaction of polymerization, polyimides derived from more basic diamines should have higher hydrolytic stability. This effect may be the reason why the more rigid copolymers based on BAPFDS have similar stability to the flexible ODADS ones; yet both perform better than BDA-type copolyimides.

It has been suggested that membranes with lower water uptake values should have better aqueous stability, but this is not the case. ODADS-type polyimides have greater water uptake than BDA-types, but the ODADS polymers show better stability performance. The flexible ether bond in ODADS may be responsible for the enhanced stability and higher water sorption in these membranes. Therefore, the stability of sulfonated six-membered ring polyimides is complex and seems directly dependent on the degree of sulfonation, the block length of the sulfonated repeat unit, and the flexibility and basicity of both the sulfonated and nonsulfonated diamines.

2.1.4. Direct Copolymerization of Sulfonated Poly(arylene ether sulfone)s

In general, post-sulfonated poly(arylene ether sulfone) copolymers, which are discussed in a later section, have one randomly placed sulfonic acid per repeat unit on the activated phenyl ring of the polymer. Also, materials derived from bisphenol A are susceptible to acid catalyzed hydrolysis. Two methods have been reported to place the sulfonic acid groups on the deactivated sites of the repeat unit. By having the sulfonic acid groups on deactivated rings, the final polymer may have improved stability and possibly higher acidity due to the electron-withdrawing sulfone group. The first method is a metalation-sulfination-oxidation process used by Kerres *et al.*, and is discussed in the Post-Sulfonation section below. However, post-functionalization of polymers is difficult to control and may lead to side reactions. An improved method was described by Ueda *et al.*, where disulfonated poly(arylene ether sulfone) copolymers were synthesized from a sulfonated monomer, 3,3'-disulfonate-4,4'-dichlorodiphenylsulfone (SDCDPS).[29] The preparation of SDCDPS was previously reported as a flame retardant additive for poly(arylate)s.[30] Ueda *et al.* reported the general conditions for the sulfonation of 4,4'-dichlorodiphenylsulfone (DCDPS) to SDCDPS; however, the potential applications were not discussed. More recently, Wang et al. modified this procedure to synthesize high molecular weight wholly aromatic disulfonated poly(arylene ether sulfone) copolymers.[31] Two other sulfonated monomers for poly(arylene ether) synthesis have been reported, and are shown in Figure 2-6. The first, SDFDPS, was prepared by Wang et al. Fluorine is a better leaving group for the nucleophilic displacement reaction used for poly(arylene ether) synthesis, and allowed higher molecular weight materials to be synthesized at lower temperatures. The second monomer, sodium 5,5'-carbonylbis(2-

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[29] Ueda, M.; Toyota, H.; Ouchi, T.; Sugiyama, J.; Yonetake, K.; Masuko, T.; Teramoto, T. Synthesis and Characterization of Aromatic Poly(ether sulfone)s Containing Pendant Sodium Sulfonate Groups. *J. Polym. Sci: Part A: Polym. Chem.* **1993**, *31(4)*, 853-858.

[30] Robeson, L.M.; Matzner, M. Flame Retardant Polyarylate Compositions. Eur. Pat. Appl. 58403, 1982.

[31] Wang, F.; Ji, Q.; Harrison, W.; Mecham, J.; Glass, T.; Formato, R.; Kovar, R.; Osenar, P.; McGrath, J.E. Synthesis of Sulfonated Poly(arylene ether sulfone)s via Direct Polymerization. *ACS Div. Polym. Chem., Polym. Preprs.* **2000**, *41(1)*, 237-238.

fluorobenzenesulfonate) (SDFK) was synthesized for poly(aryl ether ketone)s.[32] Several disulfonated poly(arylene ether ketone) copolymers were prepared from SDFK, and the solubility and thermal properties of the resulting polymers are discussed.'[33]

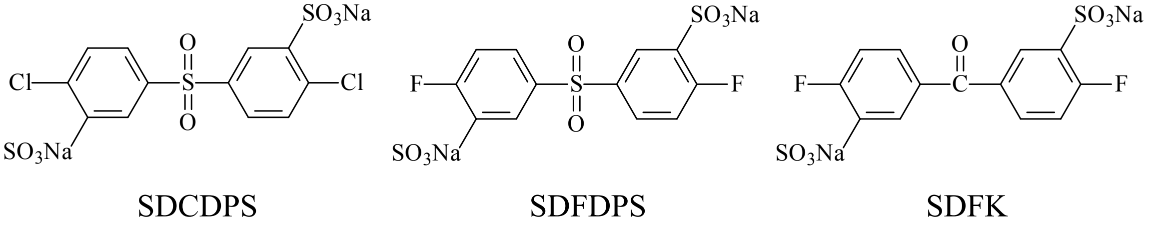

Figure 2-6. Sulfonated activated aromatic di-halide monomers for poly(arylene ether) synthesis

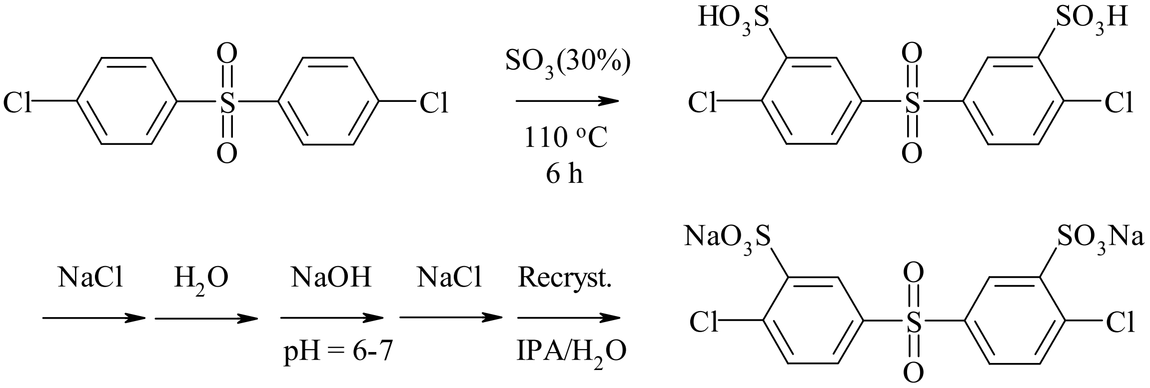

Figure 2-7. Disulfonation of 4,4'-dichlorodiphenylsulfone (DCDPS) to 3,3'-disulfonate-4,4'-dichlorodiphenylsulfone (SDCDPS)[34]

Direct copolymerization offers several advantages over the post-sulfonation reactions, including ease of control over the degree of sulfonation by varying the ratio of sulfonated to nonsulfonated monomers, degradation-free preparation, and the lack of

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[32] Wang, F.; Chen, T.; Xu, J. Sodium Sulfonate-Functionalized Poly(ether ether ketone)s. *Macromol. Chem. Phys.* **1998**, *199*, 1421-1426.

[33] Wang, F.; Li, J.; Chen, T.; Xu, J. Synthesis of Poly(ether ether ketone) with High Content of Sodium Sulfonate Groups and its Membrane Characteristics. *Polymer* **1998**, *40(3)*, 795-799.

cross-linking reactions. Wang *et al.* recently made significant progress by preparing wholly aromatic sulfonated poly(arylene ether sulfone)s by direct copolymerization.[34] These copolymers are synthesized via a high temperature nucleophilic substitution reaction of SDCDPS, DCDPS, and 4,4'-biphenol (Figure 2-8). The random wholly aromatic disulfonated copolymers were prepared with up to 1.2 sulfonic acid groups per repeat unit.[35] The copolymers are polymerized in the sulfonate salt form, cast into films and were subsequently acidified. Either a room temperature acidification method (Method 1) or a boiling acidification method (Method 2) was used to convert the sodium sulfonate groups to sulfonic acid moieties.[36] The initial degree of disulfonation was unchanged by the different acidification treatment methods. It was shown that the sulfonic acid groups were successfully introduced into the copolymers without any side reactions, and the acidification treatment did not induce any further sulfonation.

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[34] Wang, F.; Hickner, M.; Ji, Q.; Harrison, W.; Mecham, J.; Zawodzinsi, T.A.; McGrath, J.E. Synthesis of Highly Sulfonated Poly(arylene ether sulfone) Random (Statistical) Copolymers via Direct Polymerization. *Macromol. Symp.* **2001**, *175*, 387-395.

[35] Wang, F.; Hickner, M.; Kim, Y.S.; Zawodzinski, T.A.; McGrath, J.E. Direct Polymerization of Sulfonated Poly(arylene ether sulfone) Random (Statistical) Copolymers: Candidates for New Proton Exchange Membranes. *J. Membr. Sci.* **2002**, *197*, 231-242.

[36] Kim, Y.S.; Wang, F.; Hickner, M.; McCartney, S.; Hong, Y.T.; Harrison, W.; Zawodzinski, T.A.; McGrath, J.E. Effect of Acidification Treatment and Morphological Stability of Sulfonated Poly(arylene ether sulfone) Copolymer Proton-Exchange Membranes for Fuel-Cell Use Above 100 ^{o}C. *J. Polym. Sci.: Part B: Polym. Phys.* **2003**, *41*, 2816-2828.

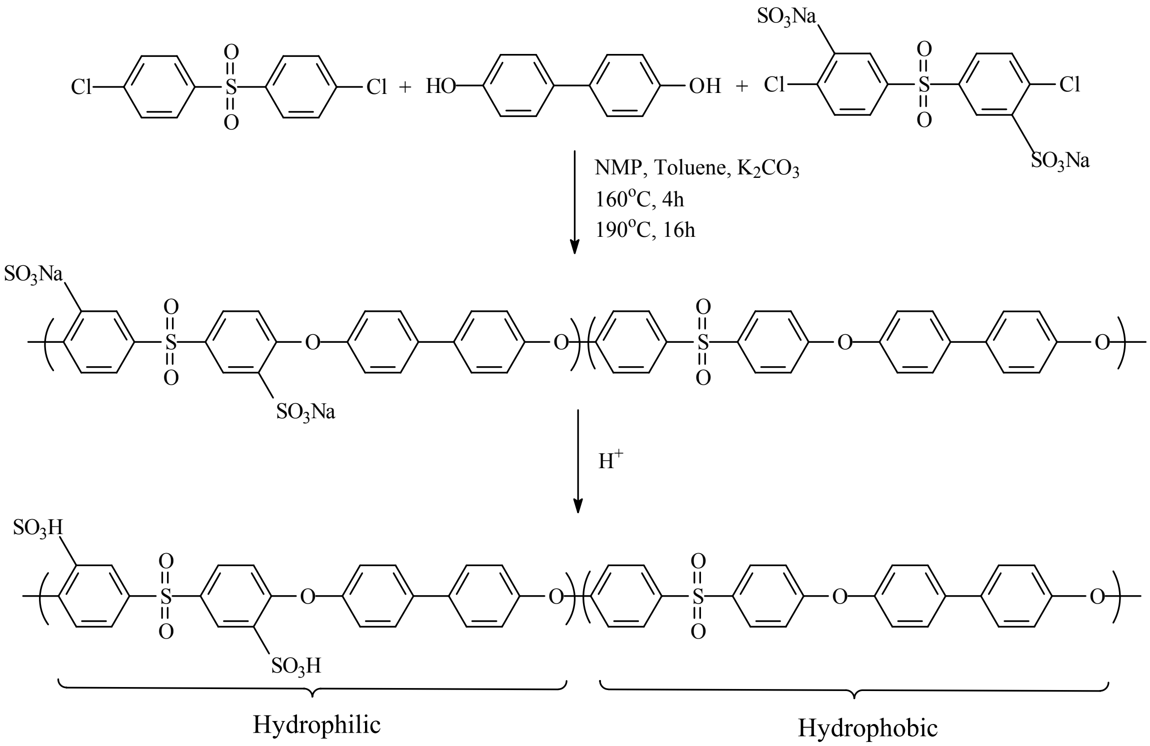

Figure 2-8. Direct copolymerization of wholly aromatic BPSH copolymers[35]

The successful introduction of sulfonic acid groups was confirmed by IEC, FT-IR, and TGA. The experimental IEC values agreed with the calculated IEC values, which were based on the molecular structure of the copolymer. The copolymers from 10-50% disulfonation have essentially no weight loss until 300 °C, a feature that compares favorably to the weight loss behavior of Nafion 1135®. DSC data showed that the sulfonic acid groups had two large effects on the glass transition temperature. An ionomer effect and an increase in molecular bulkiness of the sulfonate group caused an increase in T_g as the degree of disulfonation increased. Additionally, above 50% disulfonation for membranes prepared by Method 1, two T_gs were noticed. The water uptake, atomic force microscopy (AFM), and DSC data show that there is a percolation threshold at 50% disulfonation. By Method 1 acidification, the water uptake data increased almost linearly and then increased abruptly to 180% for 60% disulfonation. A major increase in water uptake was noted for membranes acidified by Method 2 and subsequently the percolation threshold decreased. In addition, conductivity values near or above those of Nafion® have been shown. An increase in conductivity in membranes prepared by Method 2 compared to those prepared by Method 1 was noticed. This effect may be attributed to the higher water uptake values or the more open morphology observed by AFM.

Another series of wholly aromatic copolymers from SDCDPS has been synthesized using commercially available hydroquinone in place of biphenol. These polymers exhibited higher IECs at the same degree of disulfonation, and thus higher conductivity. Although the conductivity of these polymers was enhanced, the water uptake values also increased and the percolation threshold decreased.[37]

Additional work has focused on alternate sulfonated poly(arylene ether sulfone) copolymers. Udel-type (commercial name of Solvay Advanced Polymers) sulfonated copolymers were synthesized from Bisphenol-A, SCDCDS, and DCDPS. Although these polymers were more economical due to the inexpensive Bisphenol-A monomer, the aliphatic groups may not withstand acidic and or oxidative fuel cell conditions. Utilizing Bisphenol-AF, partially fluorinated copolymers were synthesized. The introduction of fluorine into the random copolymer backbone enhanced the surface characteristics of these polymers. The fluorine groups in these copolymers self-assemble to create a highly fluorinated surface, which may make them interesting candidates for bonding to the cathode catalyst layer. Water is produced at the cathode during fuel cell operation and at the same time oxygen needs to permeate through the cathode to catalyst sites. The hydrophobicity of the fluorine-containing copolymer may help reduce water swelling in the cell.[37]

Block copolymers of BPSH and either poly(arylene ether phosphine oxide) or polyimides were prepared.[38,39] The BPSH copolymers have high water uptake values at high degrees of sulfonation that lead to a reduction in the mechanical properties. This swelling may be reduced by adding a hydrophobic block to a highly sulfonated BPSH block, while maintaining high ionic conductivity. A hydrophobic poly(arylene ether

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[37] Harrison, W.L.; Wang, F.; Mecham, J.B.; Bhanu, V.A.; Hill, M.; Kim, Y.S.; McGrath, J.E. Influence of the Bisphenol Structure on the Direct Synthesis of Sulfonated Poly(arylene ether) Copolymers. I. *J. Polym. Sci.: Part A: Polym. Chem.* **2003**, *41*, 2264 – 2276.

[38] Wang, F.; Kim, Y.; Hickner, M.; Zawodzinski, T.A. Synthesis of Polyarylene Ether Block Copolymers Containing Sulfonate Groups. *ACS Polym. Mat.: Sci. & Eng. (PMSE)* **2001**, *85*, 517-518.

phosphine oxide) (PEPO) with a molecular weight of 5,000 g/mol and hydroxyl end-groups was synthesized and characterized. Then a 100% sulfonated chlorine-terminated BPSH (BPS-100) copolymer, which also has a molecular weight 5,000 g/mol, was prepared. The PEPO was added directly to the BPS-100 polymerization to obtain a high molecular weight sulfonated block copolymer shown (Figure 2-9). Each carbon in the block copolymer showed a strong single ^{13}C NMR peak with a weak shoulder, indicating the block structure with the shoulder peak corresponding to the connecting point of the two segments.

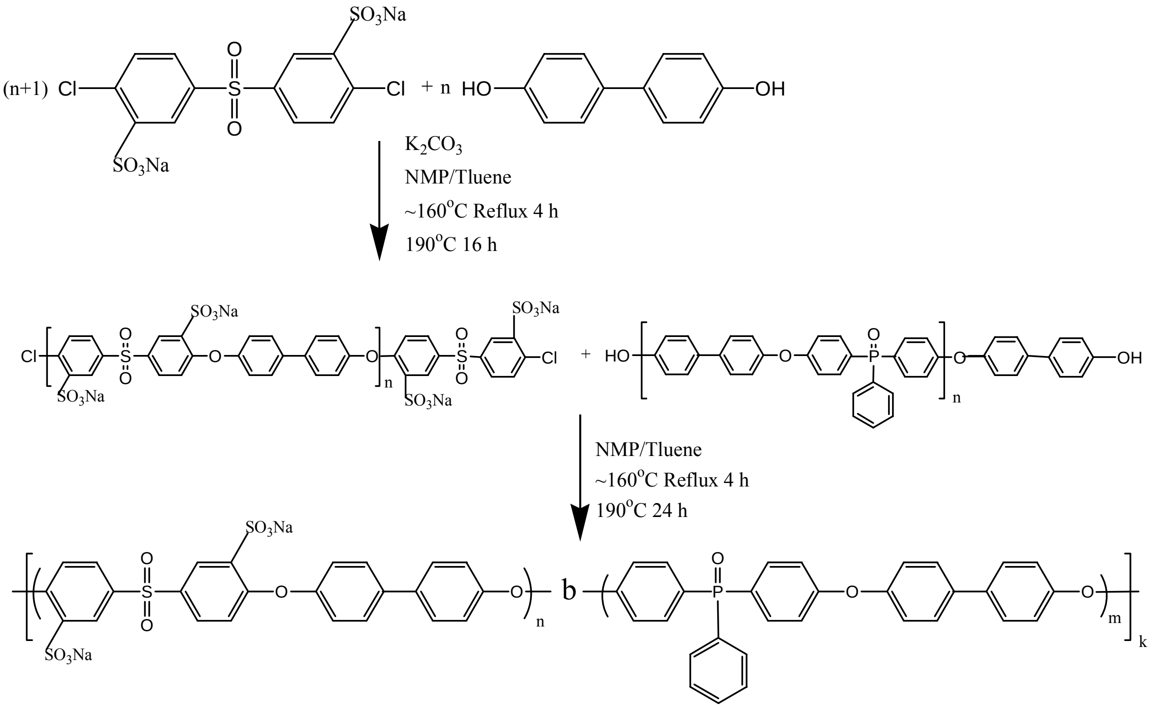

Figure 2-9. Synthesis of sulfonated poly(arylene ether sulfone)-b-poly(arylene ether phosphine oxide) (5k/5k)[38]

Several sulfonated poly(arylene ether sulfone)-block-polyimide copolymers were prepared with various block lengths.[39] In the nucleophilic substitution reaction of SDCDPS and biphenol, calculated amounts of *m*-aminophenol were added to end-cap the polymers at desired molecular weights. The molecular weight of the amine end-capped oligomers was verified by ^{1}H NMR and end-group titration. The diaminotelechelic sulfonated segment was then reacted with several dianhydrides and diamines to produce multiblock, hydrophobic polyimide-hydrophilic sulfonated polyarylene ether copolymers. A series of tough, film-forming segmented copolymers was prepared and characterized. It was concluded that the segmented or block systems have the potential to enhance certain desirable PEM characteristics in fuel cells, particularly those related to swelling, retention of mechanical strength at elevated temperatures, and critical adhesion issues in membrane electrode assemblies.

Besides sulfonated poly(arylene ether sulfone)s, sulfonated poly(arylene thioether sulfones)s and poly(phthalazinone ether sulfone)s were also synthesized.[40,41] Sulfonated poly(arylene thioether sulfone)s were prepared from SDFDPS, DFDPS, and 4,4'-thiobenzenethiol. High molecular weight copolymers were obtained and tough films of the acid form were produced. Future work includes utilizing SDCDPS as the sulfonated dihalide, studying the methanol permeability and morphological features of these

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[39] Mecham, J.B. Direct Polymerization of Sulfonated Poly(arylene ether) Random Copolymers and Poly(imide) Sulfonated Poly(arylene ether) Segmented Copolymers: New Candidates for Proton Exchange Membrane Fuel Cell Material Systems. Ph.D. Dissertation, Virginia Tech, Blacksburg, VA, 2001.

[40] Wiles, K.B.; Bhanu, V.A.; Wang, F.; McGrath, J.E. Synthesis and Characterization of Sulfonated Poly(arylene sulfide sulfone) Copolymers as Candidates for Proton Exchange Membranes. *ACS Div. Polym. Chem., Polym. Preprs.* **2002**, *43(2)*, 993-994.

[41] Wiles, K.B.; Wang, F.; McGrath, J.E. Directly Copolymerized Poly(arylene sulfide sulfone) Disulfonated Copolymers for PEM-Based Fuel Cell Systems. I. Synthesis and Characterization. *J. Polym. Sci.: Part A: Polym. Chem.* **2005**, *in press*.

polymers for comparison to the BPSH series. Sulfonated poly(phthalazinone ether sulfone) copolymers were prepared by direct copolymerization from SDFDPS, difluorodiphenylsulfone (DFDPS), and 4-(4-hydroxyphenyl)phthalazinone (HPPT).[42] The swelling of these polymers was in the range of 14.0-22.9% for 20-40% disulfonation. This low degree of swelling originates from the hydrogen bonding between hydrogen atoms of the sulfonic acid groups and the carbonyl groups of HPPT. However, the hydrolytic stability of these materials was not reported.

2.1.5. Sulfonation of Poly(arylene)s: Post-Sulfonation

2.1.5.1. Sulfonated Poly(arylene ether sulfone)s

Polysulfone (PSU) is an interesting material because of its relatively low cost, commercial availability, and processability. For these reasons and more, the sulfonation of PSU materials has been studied for many years. Commercially available polysulfones, like Udel®, were first sulfonated for desalination membranes. Possibly the first report of the sulfonation of Udel® was in the patent literature where chlorosulfonic acid was used at room temperature.[43] The possibility that chlorosulfonic acid could partially cleave the isopropylidene link or that it might undergo branching and crosslinking reactions led to a second, milder sulfonation route, using sulfur trioxide and triethyl phosphate. The SO_3/TEP treatment has been used by McGrath et al.[44] and others[45], and could minimize,

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[42] Xiao, G.; Sun, G.; Yan, D.; Zhu, P.; Tao, P. Synthesis of Sulfonated Poly(phthalazinone ether sulfone)s by Direct Polymerization. *Polymer* **2002**, *43*, 5335-5339.

[43] Quentin, J.P. Sulfonated Polyarylether Sulfones. U.S. Patent 3,709,841, January 9, 1973.

[44] Johnson, B.C.; Yilgor, I.; Tran, C.; Iqbal, M. Whightman, J.P.; Lloyd, D.R.; McGrath, J.E. Synthesis and Characterization of Sulfonated Poly(arylene ether sulfone)s. *J. Polym. Sci.: Polym. Chem. Ed.* **1984**, *22*, 721-737.

if not eliminate, possible side reactions of the sulfonation. As with PEMs, the degree of sulfonation is critical in maximizing the performance of these materials in desalination. Therefore, a ^{1}H NMR technique was used to accurately determine the degree of sulfonation. Additionally, the precautions required in handling reagents and the importance of extensive Soxhlet extraction of the product with water to remove inorganic salts was stressed. Later, a homogeneous method of sulfonation with sulfur trioxide and triethyl phosphate was proposed that led to a lower clustering of ionic groups in the polymers.[46]

In 1993, an alternative method to sulfonate commercial polyether sulfones was described by Nolte *et al.*[47] The poly(arylene ether sulfone) Udel® was sulfonated homogeneously with chlorotrimethylsilyl sulfonate, generated *in-situ* by reacting chlorosulfonic acid with trimethyl chlorosilane in 1,2-dichloroethane at room temperature. The degree of sulfonation was controlled by varying the reaction time and mole ratio of sulfonating agent to the polymer.[48] Due to the large amount of swelling in these membranes, Nolte also investigated crosslinking these polymers through the sulfonic acid groups. 1,1'-Carbonyl diimidazole was use to activate the sulfonic acid group, and was then displaced by a diamine. Both aliphatic and aromatic diamines were investigated, where the aliphatic diamines were more reactive at room temperature. As

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[45] Noshay, A.; Robeson, L.M. Sulfonated Polysulfone. *J. Appl. Polym. Sci.* **1976**, *20(7)*, 1885-1903.

[46] O'Gara, J.F.; Williams, D.J.; MacKnight, W.J.; Karasz, F.E. Random Homogeneous Sodium Sulfonate Polysulfone Ionomers: Preparation, Characterization, and Blend Studies. *J. Polym. Sci.: Part B: Polym. Phys.* **1987**, *25*, 1519-1536.

[47] Nolte, R.; Ledjeff, K.; Bauer, M.; Mulhaupt, R. Partially Sulfonated Poly(arylene ether sulfone) - A Versatile Proton Conducting Membrane Material for Modern Energy Conversion Technologies. *J. Membr. Sci.* **1993**, *83*, 211-220.

[48] Lufrano, F.; Squadrito, G.; Patti, A.; Passalacqua, E. Sulfonated Poysulfone as Promising Membranes for Polymer Electrolyte Fuel Cells. *J. Appl. Polym. Sci.* **2000**, *77*, 1250-1257.

expected, a decrease in conductivity, swelling, and permselectivity was noticed for the crosslinked membranes. The reduction in conductivity was due to the loss of ion-conducting sites (sulfonic acid groups); though the membrane was still within range for use as a proton exchange membrane.

The chlorosulfonation of other polysulfones was also reported.[49] High molecular weight poly(arylene ether sulfone)s were achieved using the nucleophilic aromatic substitution reaction of Bisphenol-AF or biphenol with dichlorodiphenylsulfone in NMP. Both polymers were dissolved in an appropriate solvent and sulfonated by two methods; (1) chlorosulfonic acid only and (2) the *in-situ* chlorotrimethylsilyl sulfonate procedure used by Nolte. The results showed that the degree of sulfonation was difficult to control; however, the degree of sulfonation throughout the polymer chains was consistent. Additionally, similar results were obtained for both sulfonation methods which suggest that trimethyl chlorosilane may only be needed for sulfonation of polymers with aliphatic groups.

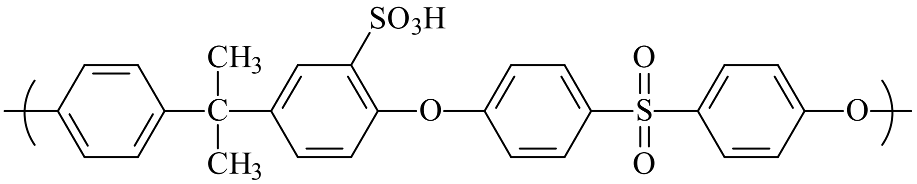

Figure 2-10. Sulfonated Udel® polysulfone generated by post-sulfonation reaction[47]

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[49] Harrison, W.L.; O'Connor, K.; Arnett, N.; McGrath, J.E. Homogeneous Synthesis and Characterization of Sulfonated Poly(arylene ether sulfone)s via Chlorosulfonic Acid. *ACS Div. Polym. Chem., Polym. Preprs.* **2002**, *43(2)*, 1159.

While both the chlorosulfonic acid and the complex of sulfur trioxide and triethlyphosphate routes produce sulfonated polymers, they lack control. Johnson and colleagues studied the substitution position of the sulfonate group. It was found that the sulfonation only occurs in the Bisphenol A aromatic ring at the activated position ortho to the ether linkage and only yields mono-substitution per repeat unit, in contrast to the diarylsulfone portion of the monomer repeat unit which has a low electron-density due to the electron withdrawing sulfone group. One disadvantage of these routes is that a sulfonic acid attached to an activated ring, like Bisphenol A, can undergo an *ipso*-substitution with H^+, therefore lowering the hydrolytic stability of the sulfonated polymer in strong acids. In an effort to increase the hydrolytic stability of sulfonated Udel PSU, Kerres and colleagues developed a novel method to attach sulfonic acids at the position ortho to the sulfone group (Figure 2-11).[50] The electron-deficient portion of the backbone can first be lithiated, and then converted to the proton-conducting sulfonic acid site. By this method, all polymers that form soluble lithium salts can be subjected to this sulfonation process, the sulfonic acid groups are introduced in the more hydrolysis-stable part of the backbone, and no chlorinated hydrocarbon solvents are necessary.

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[50] Kerres, J.; Cui, W.; Reichle, S. New Sulfonated Engineering Polymers via the Metalation Route. I. Sulfonated Poly(ether sulfone) PSU Udel® via Metalation-Sulfination-Oxidation. *J. Polym. Sci.: Part A: Polym. Chem.* **1996**, *34*, 2421-2438.

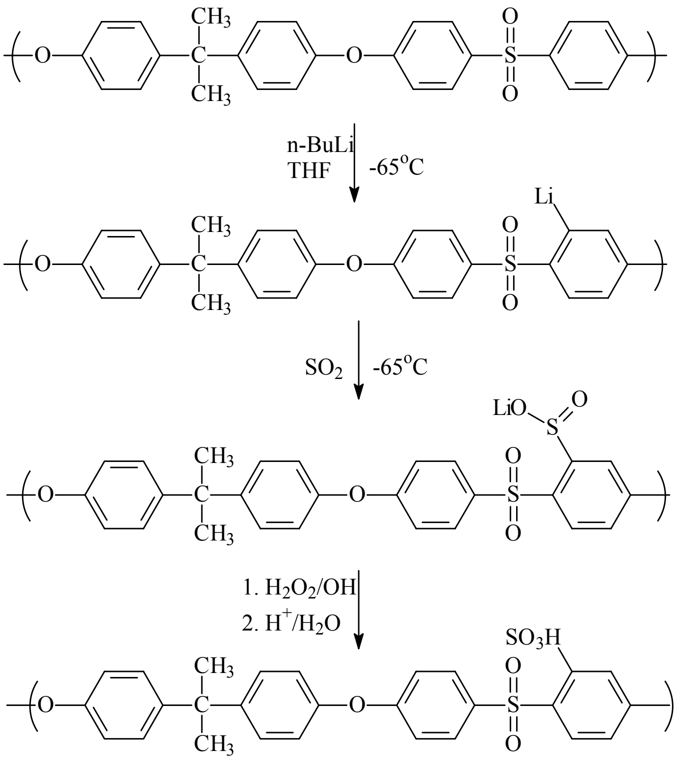

Figure 2-11. Sulfonation of poly(ether sulfone) Udel® PSU via the metalation route[50]

A more controlled method of sulfonating poly(arylene ether)s is to incorporate moieties along the polymer chain that will preferentially sulfonate. For example, to sulfonate the electron-deficient polymer Victrex PES, a more reactive sulfonating agent like sulfur trioxide needs to be used. Chlorosulfonic acid treatments will not sulfonate this material. Al-Omran and Rose prepared several poly(arylene ether sulfone)s by reacting 4,4'-dichlorodiphenylsulfone, durohydroquinone, and hydroquinone under basic conditions in the presence of potassium carbonate.[51] The molar ratios of hydroquinone to durohydroquinone were varied. Durohydroquinone has a similar structure to hydroquinone, though the four hydrogen atoms attached to the phenyl ring are replaced by methyl groups. These polymers were then sulfonated in sulfuric acid. Based on the structure of the polymer, it should only sulfonate at the ether-phenyl-ether (hydroquinone) portions of the chain. Ideally, the degree of sulfonation should be easily controlled by incorporating different amounts of hydroquinone; however, this was not the case. The polymer also partially sulfonated on the phenyl ring meta to the sulfone linkage.

Several poly(arylene ether)s with pendent phenyl rings have been prepared and either sulfonated or phosphonated.[52,53,54,55] Using pendent phenyl rings within the main

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[51] Al-Omran, A.; Rose, J.B. Synthesis and Sulfonation of Poly(phenylene ether ether sulfone)s Containing Methylated Hydroquinone Residues. *Polymer* **1996**, *37*, 1735-1743.

[52] Miyatake, K.; Oyaizu, K.; Tsuchida, E.; Hay, A.S. Synthesis and Properties of Novel Sulfonated Arylene Ether/Fluorinated Alkane Copolymers. *Macromolecules* **2001**, *34*, 2065-2071.

[53] Miyatake, K.; Hay, A.S. Synthesis of Novel Phosphinic Acid-Containing Polymers. *J. Polym. Sci.: Part A: Polym. Chem.* **2001**, *39*, 1854-1859.

[54] Miyatake, K.; Hay, A.S. Synthesis and Properties of Poly(arylene ether)s Bearing Sulfonic Acid Groups on Pendant Phenyl Rings. *J. Polym. Sci.: Part A: Polym. Chem.* **2001**, *39*, 3211-3217.

[55] Miyatake, K.; Hay, A.S. New Poly(arylene ether)s with Pendant Phosphonic Acid Groups. *J. Polym. Sci.: Part A: Polym. Chem.* **2001**, *39*, 3770-3779.

chain of the polymer will direct the post-sulfonation reaction so that the sulfonic acid substituents are attached onto the pendent phenyl groups. These sulfonic acid groups are reportedly more stable under fuel cell conditions than those attached on the main chain, with respect to those polymers that are post-sulfonated, where the sulfonic acid group is attached to the activated phenyl ring of the polymer chain. The polymers were sulfonated with chlorosulfonic acid in methylene chloride at room temperature for several hours. The degree of sulfonation was dependent on the sulfonation time.

Copolymers including fluorinated alkane moieties in addition to the bulky phenyl rings have shown relatively high proton conductivity (>10^{-3} S/cm), however, these polymers generally show substantial swelling in methanol. Their use in direct methanol fuel cells would probably be limited because the fluoroalkanes, like Nafion®, have high affinity to methanol, causing crossover of the fuels. Therefore, wholly aromatic systems were also synthesized to produce thermally and hydrolytically stable sulfonated polymers with low methanol affinity. Although the authors do not give any methanol crossover data, these wholly aromatic sulfonated poly(arylene ether)s did not swell in methanol like the fluorinated alkanes. No conductivity data was given for these polymers; however, they are insoluble in water and TGA data showed the presence of sulfonic acid groups.

Despite their potential usefulness, phosphonic or phosphinic acid-containing polymers for PEMFCs have not been well studied. The reason for this is most likely due to their rather limited synthetic procedures available in the literature compared to sulfonic acid derivatives. By using carbamoyl-masking groups to improve the nucleophilic substitution reaction polymerization, high molecular weight phosphinic acid containing poly(arylene ether) copolymers were synthesized. However, little information was given on their properties as PEMs. Additionally, polymers similar to the wholly aromatic poly(arylene ether)s above were synthesized and phosphonic acid groups were attached to the pendent phenyl rings. Long reaction times of about 70 hours were needed for the complete phosphonation reaction. The phosphonic acid-containing polymers produced tough, ductile films indicating that they could potentially serve as proton exchange membranes.

Recently, phosphonated poly(arylene ether sulfone) copolymers were prepared via lithiation and then reaction with chlorophosphonic acid esters (Figure 2-12).[56] Organolithium compounds were used because these compounds generally minimize side-products that may occur in phosphonation reactions. Since the lithiation process is an electrophilic substitution, the reaction took place on the most electron-deficient carbons of the polymer backbone. In the case of Udel, phosphonic acid sites were attached to the deactivated benzene rings ortho to the sulfone linkages. The authors were also able to phosphonate polysulfone on the activated benzene rings by bromination of Udel. The brominated sites located ortho to the ether linkages were selectively metalized in a second step because the halogen-lithium step is favored of the proton-lithium exchange at low temperatures. The authors characterized the copolymers well by conventional polymer methods (FT-IR, NMR, TGA and DSC), however, little was reported on the characteristics of the membranes important to PEMFCs.

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[56] Lafitte, B.; Jannasch, P. Phosphonation of Polysulfones via Lithiation and Reaction with Chlorophosphonic Acid Esters. *J. Polym. Sci.: Part A: Polym. Chem.* **2005**, *43*, 273-286.

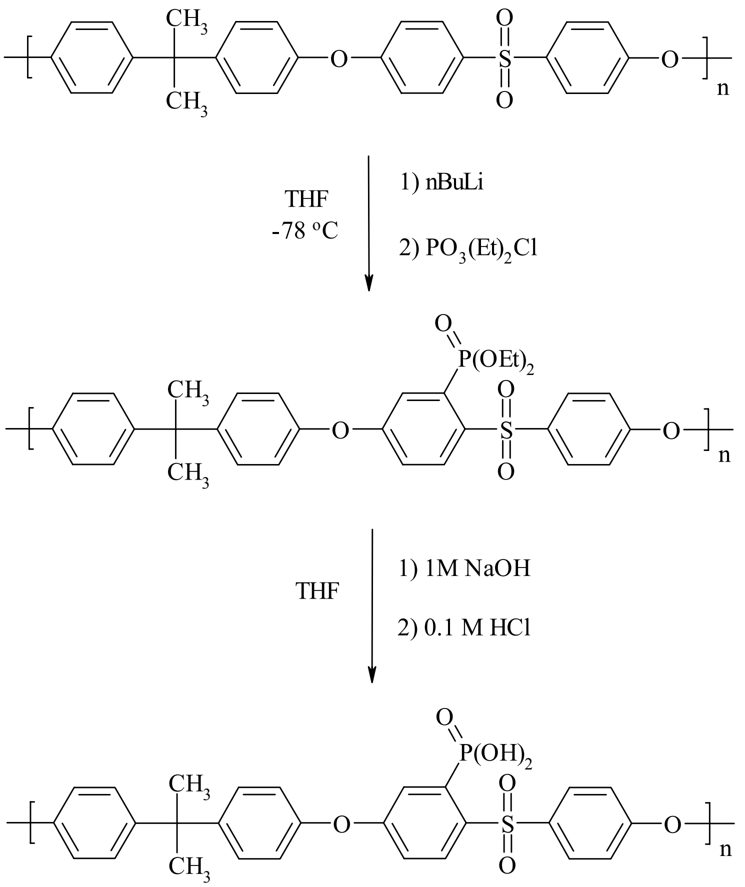

Figure 2-12. Phosphonation of poly(ether sulfone) Udel® PSU via the metalation route[56]

2.1.5.2. Sulfonated Poly(ether ketone)s

Poly(ether ether ketone) (PEEK) is an aromatic high-performance, semicrystalline polymer based on hydroquinone and 4,4'-difluorobenzophenone with extremely good thermal stability, chemical resistance, and electrical and mechanical properties. Due to the crystallinity in PEEK, this polymer shows little solubility in organic solvents. One of the first methods to characterize PEEK was by sulfonating the parent polymer. By adding sulfonic acid groups to the backbone, the crystallinity decreased and solubility increased. Sulfonation of PEEK with chlorosulfonic acid or fuming sulfuric acid causes degradation of the polymer; therefore concentrated sulfuric acid is typically used. The sulfonation rate of PEEK in sulfuric acid is a heterogeneous reaction but was controlled by changing the reaction time, temperature and the acid concentration to provide polymers with a sulfonation range of 30 to 100%, without apparent degradation or crosslinking reactions.[57] However, sulfonation of PEEK in sulfuric acid cannot be used to produce truly random copolymers at sulfonation levels less than 30% because dissolution and sulfonation occur in a heterogeneous environment.[58] The sulfonation of PEEK is a second-order reaction, which preferentially takes place at the aromatic ring flanked by two ether links, due to the higher electron density of the ring (Figure 2-13). Since the electron density of the other two aromatic rings in the repeat unit is relatively low due to the electron-attracting nature of the neighboring ketone group, one sulfonic acid group adds per repeat unit.

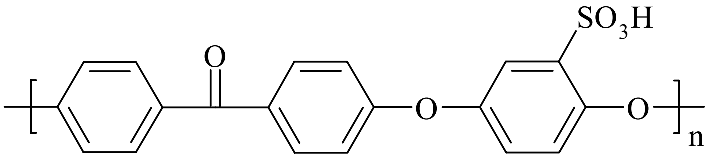

Figure 2-13. Sulfonated poly(ether ether ketone) (PEEK)

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[57] Huang, R.Y.M.; Pinghai Shao, C.M.; Burns, X.; Feng, X. Sulfonation of Poly(ether ether ketone) (PEEK): Kinetic Study and Characterization. *J. Appl. Polym. Sci.* **2001**, *82*, 2651-2660.

[58] Bailly, C.; Williams, D.J.; Karasz, F.E.; MacKnight, W.J. The Sodium Salts of Sulphonated of Poly(aryl-ether-ether-ketone) (PEEK): Preparation and Characterization. *Polymer* **1987**, *28*, 1009-1016.

2.1.5.3. Sulfonated Substituted Poly(arylene)s

Several types of poly(arylene)s have been sulfonated in the literature. Recently, substituted poly(*p*-phenylene)s were sulfonated,[59], [60] and sulfonated poly(*p*-phenylene)/poly(ether sulfone) block copolymers were prepared.[61] The sulfonation was achieved using fuming sulfuric acid at room temperature. The amount of sulfonic acid groups in the polymer was controlled by varying the reaction time. Highly conductive polymers (0.1 S/cm) were obtained within 60 minutes of the sulfonation reaction, after which the polymers were water soluble.

Poppe *et al* synthesized novel soluble copolyarylenes via a Ni(0)-catalyzed coupling reaction of aryl chlorides..[62] Molar ratios of 4,4'-dichlorodiphenylsulfone to *m*-dichlorobenzene were used to vary the amount of *m*-phenylene in the final copolymer. Then these copolymers were sulfonated in chlorosulfonic acid. Due to the electron-withdrawing nature of the sulfone group, the copolymers only sulfonated at the phenyl ring that is not next to the sulfone. Therefore, the degree of sulfonation could be controlled by the amount of *m*-dichlorobenzene included in the polymerization. Solution-cast transparent membranes of these materials displayed higher water sorption and proton conductivities compared to Nafion 117.

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[59] Ghassemi, H.; McGrath, J.E. Proton-Conducting Polymers Derived From Poly(p-phenylene)s. *ACS Div. Polym. Chem., Polym. Preprs.* **2002**, *43(2)*, 1021-1022.

[60] Ghassemi, H.; McGrath, J.E. Synthesis and Properties of New Sulfonated Poly(*p*-phenylene) Derivatives for Proton Exchange Membranes. I. *Polymer* **2004**, *45*, 5847-5854.

[61] Ghassemi, H.; Ndip, G.; McGrath, J.E. New Multiblock Copolymers of Sulfonated Poly(4'-phenyl-2,5-benzophenone) and Poly(arylene ether sulfone) for Proton Exchange Membranes. II. *Polymer* **2004**, *45*, 5855-5862.

[62] Poppe, D.; Frey, H.; Kreuer, K.D.; Heinzel, A.; Mulhaupt, R. Carboxylated and Sulfonated Poly(arylene-co-arylene sulfone)s: Thermostable Polyelectrolytes for Fuel Cell Applications. *Macromolecules* **2002**, *35*, 7936-7941.

A disadvantage of the poly(phenylene)s described above is that only one sulfonic acid group was attached per repeat unit. Alternatively, poly(phenylene)s prepared by a Diels-Alder method have been sulfonated with up to three sulfonic acid sites per repeat unit.[63] The sulfonated poly(phenylene)s were prepared by a Diels-Alder reaction of bis(tetracyclone) with *p*-bis(ethynyl)benzene, followed by post-sulfonation. These materials have improved solubility, thermal stability and proton conductivities compared to previously reported poly(phenylene)s.

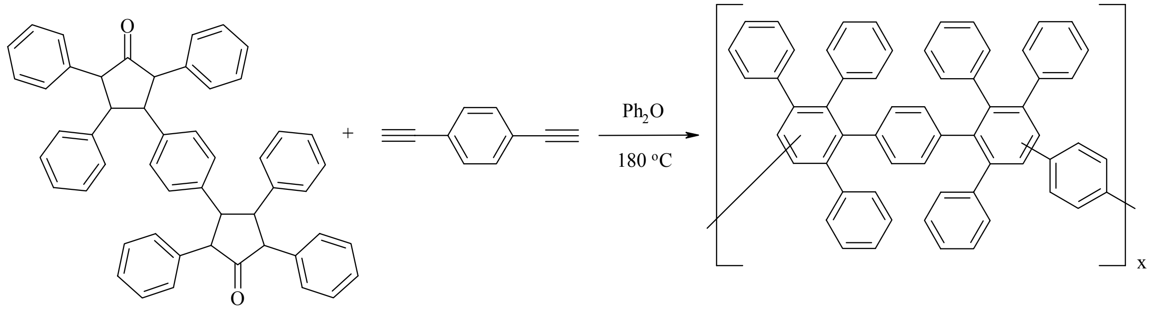

Figure 2-14. Synthesis of Diels-Alder poly(phenylene)s[63]

2.1.6. Sulfonated Polybenzazoles

Polybenzazoles are characterized by their five-membered heterocyclic ring shown in Figure 2-15, where X = NH for polybenzimidazoles, X = O for polybenzoxazoles and X = S for polybenzothiazoles. These polymers can be synthesized from the reaction of dicarboxylic acids with tetramines, bis(*o*-aminophenol)s, or bis(*o*-aminothiophenol)s, respectively, in polyphosphoric acid. Polybenzimidazoles doped with phosphoric acid have been extensively studied as candidates for proton exchange membrane (PEM) fuel

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[63] Fujimoto, C.H.; Cornelius, C.J. Application of Sulfonated Diels-Alder Polyphenylenes in Hydrogen Based PEM Fuel Cells. *ACS Fuel Chem. Div. Prepr.* **2003**, *48(2)*, 889.

cells.[64] The basic nature of the imidazole ring promotes interactions with strong acids such as HBr, H_2SO_4, and H_3PO_4.[65,66] In particular, PBI can incorporate significant amounts of phosphoric acid even from dilute aqueous solutions.[67] However, there are only a few accounts describing the synthesis of sulfonated polybenzimidazole, or any type of sulfonated polybenzazole.

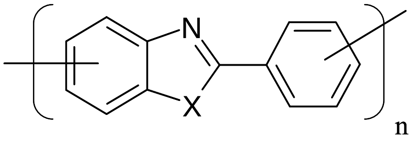

Figure 2-15. Chemical structure of polybenzazoles where X = NH for polybenzimidazoles, X = S for polybenzothiazoles and X = O for polybenzoxazoles

Benicewicz et al. described a novel method to load PBI membranes with high levels of phosphoric acid.[68] Polybenzimidazoles were prepared in polyphosphoric acid, directly cast from the polymerization solvent, and then the polyphosphoric acid was hydrolyzed to phosphoric acid in a sol-gel process. The resulting membranes showed

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[64] Wainright, J.S.; Wange, J.T.; Weng, D.; Savinell, R.F.; Litt, M. Acid-Doped Polybenzimidazole: A New Polymer Electrolyte. *J. Electrochem. Soc.* **1995**, *142(7)*, L121-L123.

[65] Schuster, M.F.H.; Meyer, W.H. Anhydrous Proton-Conducting Polymers, *Annu. Rev. Mater. Res.* **2003**, *33*, 233-261.

[66] Bouchet, R.; Sieber, E. Proton Conduction in Acid Doped Polybenzimidazole. *Solid State Ionics* **1999**, *118(3-4)*, 287-299.

[67] Glipa, X.; Bonnet, B.; Mula, B.; Jones, D.J.; Roziere, J. Investigation of the Conduction Properties of Phosphoric and Sulfuric Acid Doped Polybenzimidazole. *J. Mater. Chem.* **1999**, *9(12)*, 3045-3049.

[68] Xiao, L.; Zhang, H.; Choe, E.-W.; Scanlon, E.; Ramanathan, L.S.; Benicewicz, B.C. PBI Polymers for High-Temperature PEM Fuel Cells. *Abstracts of Papers,* Advances in Materials for Proton Exchange Membrane Fuel Cell Systems, Pacific Grove, CA, Feb 23-26, 2003; Preprint Number 10.

inherently high proton conductivities even at low humidity, presumably due to the high acid doping levels.[69]

In 1977, Uno et al. prepared sulfonated polybenzimidazoles from aromatic tetraamines and either 2-sulfoterephthalic acid or disulfoisophthalic acid.[70] The polymers were synthesized with the sulfonic acid groups *meta* to the carbon of the benzimidazole ring in an effort to prepare ladder polymers. It was thought that the sulfonic acid sites would cyclodehydrate to sulfones due to the interaction with the proton of the imidazole ring. However, the polymers gave polybenzimidazoles above 400 ^{o}C by eliminating sulfonic acid groups, instead of ring closure.

Several other groups have prepared sulfonated polybenzimidazoles by direct polymerization of sulfonated disulfoterephthalic acid, 2-sulfoterephthalic acid and 5-sulfoisophthalic acid.[71,72,73,74] 5-Sulfoisophthalic acid is an attractive monomer for preparation of sulfonated polymers because it is commercially available and relatively inexpensive. Asensio et al. investigated phosphoric acid doped polybenzimidazoles with

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[69] Xiao, L.; Zhang, H.; Choe, E,-W.; Scanlon, E.; Ramanathan, L.S.; Benicewicz, B.C. Synthesis and Characterization of Pyridine-Based Polybenzimidazoles as Novel Fuel Cell Membrane Materials. *Fuel Chem. Div. Prepr.* **2003**, *48(1)*, 447-448.

[70] Uno, K.; Niume, K.; Iwata, Y.; Toda, F.; Iwakura, Y. Synthesis of Polybenzimidazoles with Sulfonic Acid Groups. *J. Polym. Sci.: Polym. Chem. Ed.* **1977**, *15*, 1309-1318.

[71] Asensio, J.A.; Borros, S.; Gomez-Romero, P. Proton-Conducting Polymers Based on Benzimidazoles and Sulfonated Benzimidazoles. *J. Polym. Sci.: Part A: Polym. Chem.* **2002**, *40*, 3703-3710.

[72] Sakaguchi, Y.; Kitamura, K.; Nakao, J.; Hamamoto, S.; Tachimori, H.; Takase, S. Preparation of Sulfonated or Phosphonated Polybenzimidazoles and Polybenzoxazoles. *ACS Polym. Mat.: Sci. & Eng. (PMSE)* **2001**, *84*, 899-900.

[73] Reynolds, J.R.; Lee, Y.; Kim, S.; Bartling, R.L.; Gieselman, M.B.; Savage, C.S. Rigid-Rod and High Ratio Aromatic Polyelectrolytes based on Polybenzimidazoles and Polybenzothiazoles. *ACS Div. Polym. Chem., Polym. Preprs.* **1993**, *34(1)*, 1065-1066.

[74] Venkatasubramanian, N.; Dang, T.D.; Vance, T.A.; Arnold, F.E. Rigid-Chain Polymers with Two Sulfonic Acid Pendents. *ACS Polym. Mat.: Sci. & Eng. (PMSE)* **2001**, *84*, 601-602.

and without sulfonic acid groups present. Their results demonstrated that the nonsulfonated polybenzimidazoles can be doped with more phosphoric acid. However, when comparing polymers with the same amount of phosphoric acid, the PBIs with pendent sulfonic acids had higher conductivity under hydrated conditions. This finding can be attributed to the higher acidity of the sulfonic acid group.

The synthesis of sulfonated poly(benzothiazoles)[75] and polybenzoxazoles,[76] by direct polymerization of sulfonated diacid monomers was reported. The sulfonated poly(benzothiazole)s and polybenzoxazoles were synthesized in polyphosphoric acid and completely characterized by NMR, FT-IR, and thermal analysis. The proton conductivities of the sulfonated polybenzoxazoles were in the range of 10^{-3} to 10^{-1} S/cm at 80 ^{o}C and 95% relative humidity.

2.1.7. Proton-Conducting Polyphosphazenes

Polyphosphazenes with appropriate proton-conducting sites have been synthesized as materials for PEMs. The combination of a stable inorganic backbone with the ability to achieve high ionic exchange capacities (~ 2 meq/g) suggests that they are good candidates for PEMFCs.[77] Moreover, their synthesis by macromolecular substitution allows the properties to be tuned over a wide range of structures, including lower methanol diffusion in DMFCs. Typically, high molecular weight

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[75] Kim, S.; Cameron, D.A; Lee, Y.; Reynolds, J.R.; Savage, C.R. Aromatic and Rigid Rod Polyelectrolytes based on Sulfonated Poly(benzobisthiazole)s. *J. Polym. Sci.: Part A: Polym. Chem.* **1996**, *34*, 481-492.

[76] Sakaguchi, Y.; Kitamura, K.; Nakao, J.; Hamamoto, S.; Tachimori, H.; Takase, S. *Preparation and Properties of Sulfonated or Phosphonated Polybenzimidazoles and Polybenzoxazoles*, in Carraher, C.E.; Swift, G. (Eds.), Functional Condensation Polymers, Kluwer, New York, NY, 2002, pp. 95 – 104.

[77] Guo, Q.; Pintauro, P.N.; Tang, H.; O'Connor, S. Sulfonated and Crosslinked Polyphosphazene-Based Proton-Exchange Membranes. *J. Membr. Sci.* **1998**, *154*, 175-181.

poly(dichlorophosphazene) (PDCP) is synthesized via ring opening polymerization, and then functionalized through nucleophilic substitution of the chlorine atoms. Sulfonation of the substituted phenyl rings on polyphosphazene has been achieved using SO_3, sulfuric acid, and even fuming sulfuric acid.[78] As with many post-sulfonation procedures, this method suffers from irregularities in the polymer structure, poor control over the ion exchange capacity and heterogeneity in the reaction mixture.

It would be advantageous to design a one-step procedure to replace the chlorine atoms of the polymer with a sulfonic acid-containing nucleophile to increase control over the polymer composition. However, the sodium salt of 4-hydroxybenzenesulfonic acid is not a suitable reagent for the substitution due to crosslinking and degradation of the polymer. The sodium sulfonate sites preferentially react before the phenoxide producing an insoluble material. In an attempt to suppress the reactivity of aryl sulfonates, 4-hydroxybenzenesulfonate was converted to a hydrophobic ammonium salt by reacting it with dimethyldipalmitylammonium bromide.[79] When this hydrophobic ammonium salt was reacted with PDCP, the result was degradation-free high molecular weight sulfonated polyphosphazene. The protecting groups were easily removed by treatment with base and precipitation in methanol. These results indicate that this "direct sulfonation" route can be effectively performed without noticeable side reactions.

Alternative proton-conducting polyphosphazenes have been prepared with pendent phenyl phosphonic acid and sulfonimide groups. These acid groups are

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[78] Wycisk, R.; Pintauro, P.N. Sulfonated Polyphosphazene Ion Exchange Membranes. *J. Membr. Sci.* **1996**, *199*, 155-160.

[79] Adrianov, A.K.; Marin, A.; Chen, J.; Sargent, J.; Corbett, N. Novel Route to Sulfonated Polyphosphazenes: Single-Step Synthesis Using "Noncovalent Protection" of Sulfonic Acid Functionality. *Macromolecules* **2004**, *37*, 4075-4080.

attractive because they are essentially non-nucleophilic in the substitution reactions. Phenyl phosphonic acid-functionalized polyphosphazenes were synthesized by first preparing polyphosphazenes with bromo-phenoxy side groups. The bromine atoms were displaced by treatment with *t*-butyllithium followed by diphenyl chlorophosphate. The resulting diphenyl phosphonate ester groups were hydrolyzed in base and then treated with acid to produce the proton-conducting phenyl phosphonic acid sites. These phosphonated polyphosphazene membranes achieved proton conductivities up to 0.05 S/cm with methanol permeabilities much lower than Nafion and comparable sulfonated polyphosphazenes. Although the proton conductivities of the phosphonated membranes were lower than equivalent sulfonated polyphosphazenes and Nafion 117, the lower methanol permeability results in higher selectivities over a range of temperatures (Figure 2-16).[80]

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[80] Zhou, X.; Weston, J.; Chalkova, E.; Hoffman, M.A.; Amber, C.M.; Allcock, H.R.; Lvov, S.N. High Temperature Transport Properties of Polyphosphazene Membranes for Direct Methanol Fuel Cells. *Electrochim. Acta* **2003**, *48*, 2173-2180.

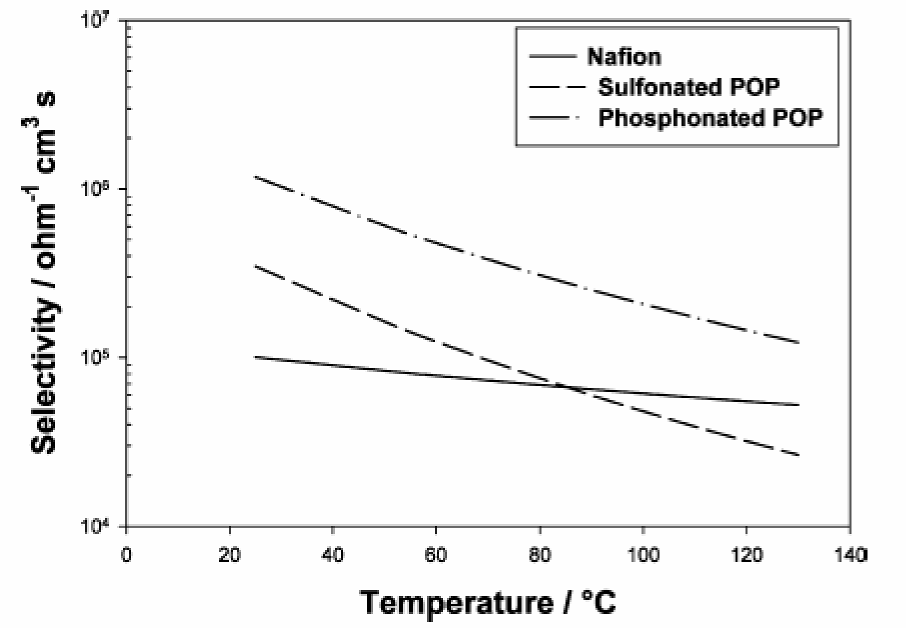

Figure 2-16. The selectivity of Nafion and proton-conducting polyphosphazene copolymers at various temperatures[80]

Highly acidic sulfonimide sites were introduced to the phosphazene backbone via nucleophilic substitution of PDCP with $NaOC_6H_4SO_2NNaSO_2CF_3$.[81] The proton conductivity of the sulfonimide-functionalized polyphosphazenes was greater than the sulfonic acid-functionalized polyphosphazene, probably due to the increased acidity of the ionic group. However, the sulfonimide materials also had higher water sorption values. At an IEC of ~0.99 meq/g, the sulfonimide copolymer swelled more than 100%. Therefore, it was necessary to crosslink these membranes or prepare blends with PVDF for them to be effective as PEMs.

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[81] Hoffman, M.A.; Amber, C.M.; Maher, A.E.; Chalkova, E.; Zhou, X.Y.; Lvov, S.N.; Allcock, H.R. Synthesis of Polyphosphazenes with Sulfonimide Side Groups. *Macromolecules* **2002**, *35*, 6490-6493.

2.1.8. Inorganic Additives

The incorporation of inorganic components in polymer electrolyte materials improves several key PEM properties, including water retention, proton conductivity, mechanical integrity and methanol crossover.[82] A simple technique to prepare inorganic composite membranes is by casting an ionomer solution containing one or more inorganic components. Heteropolyacids (HPA) are ideal for solution casting because most are soluble in typical casting solvents (NMP, DMAc, etc.), highly conductive when hydrated, and are available. HPAs are a large and diverse class of polyoxometallates that can act as redox catalysts when substituted by a transition metal, are proton conductors, and can be reduced to form electronically conducting materials, ideal candidates for an electrode material in a PEM fuel cell. HPAs typically exist in hydrated phases, with the degree of hydration ranging from 6 to 29 hydrated water molecules depending on temperature and relative humidity. Similarly, the proton conductivities of HPAs vary from 6×10^{-5} to 1.8×10^{-2}, depending on the amount of water present.

One of the major drawbacks of Nafion is its inherently poor fuel cell performance above 100 ^{o}C due to reduced proton conductivity at low relative humidity and hydrated glass transition temperature. Nafion/HPA composite membranes have been investigated for high temperature hydrogen/air fuel cell applications to improve water retention above the boiling point of water.[83] Several HPAs (phosphotungstic acid, silicotungstic acid, phosphomolybdic acid, and silicomolybdic acid) had very little effect on the water uptake

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[82] Alberti, G.; Casciola, M. Composite Membranes for Medium-Temperature PEM Fuel Cells. *Annu. Rev. Mater. Res.* **2003**, *33*, 129-154.

[83] Tazi, B.; Savadago, O. Parameters of PEM Fuel-Cells Based on New Membranes Fabricated from Nafion. *Electrochimica Acta* **2000**, *45*, 4329-4339.

of Nafion; however, the proton conductivity improved at low relative humidity.[84] Yet the long-term stability of these water-soluble HPAs in Nafion was not investigated.

Kim et al. studied the incorporation of phosphotungstic acid in BPSH membranes at various levels of disulfonation.[85] These composite membranes had lower HPA extraction levels than Nafion and displayed improved mechanical properties, thermal stability and glass transition temperatures. Incorporation of HPA into the disulfonated copolymer significantly reduced the water swelling behavior, without influencing the proton conductivity at room temperature. Nevertheless, the composite membranes showed greater increases in proton conductivity at elevated temperatures (100 – 130 ^{o}C), which suggests that these membranes are good candidates for high temperature fuel cell operation.

Another method to prepare inorganic composite PEMs is by an exchange-precipitation process, which is typically used to prepare metal(IV) acid phosphates and phosphonates. A good example of this process for the preparation of zirconium hydrogen phosphate is given. The membrane is swollen in boiling water then transferred to a zirconyl chloride solution at 80 ^{o}C. Thus, the Zr^{4+} ions are introduced into the hydrophilic portion of the membrane and can subsequently precipitate to form zirconium phosphate nanoparticles upon immersion in a phosphoric acid solution. A major advantage of zirconium hydrogen phosphate over HPA is that it is water insoluble, and therefore will not leach out under fuel cell conditions. This method has been used in our

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[84] Ramani, V.; Kunz, H.R.; Fenton, J.M. Investigation of Nafion/HPA Composite Membranes for High Temperature/Low Relative Humidity PEMFC operation. *J. Membr. Sci.* **2004**, *232*, 31-44.

[85] Kim, Y.S.; Wang, F.; Hickner, M.; Zawodzinski, T.A.; McGrath, J.E. Fabrication and Characterization of Heteropolyacid ($H_3PW_{12}O_{40}$)/Directly Polymerized Sulfonated Poly(arylene ether sulfone) Copolymer Composite Membranes for Higher Temperature Fuel Cell Applications. *J. Membr. Sci.* **2003**, *212*, 263-282.

group with BPSH copolymers to improve the mechanical properties, high temperature proton conductivity and DMFC performance of the resulting composite membranes.[86,87]

Similarly, zirconium hydrogen phosphate has been incorporated into Nafion to study its effect on the membrane properties. Zirconium hydrogen phosphate/Nafion composite membranes had higher water sorption values and lower proton conductivities over a range of water activities when compared to a pure Nafion membrane.[88] Even though the Nafion membranes showed higher proton conductivities, the fuel cell performance of the composite membranes exceeded that of Nafion at high temperature (130 ^{o}C). Inorganic additives in composite membranes have the possibility of generating performance that pure organic polymer membranes cannot achieve. Though, the type of additive, amount, size and orientation of the solid particles dispersed in the polymer matrix must still be examined.

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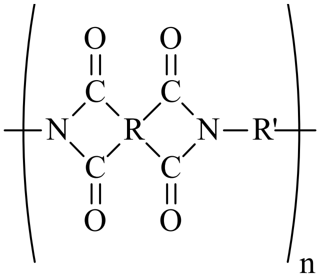
[86] Hickner, M.A. Transport and Structure in Fuel Cell Proton Exchange Membranes. Ph.D. Dissertation, Virginia Tech, Blacksburg, VA, 2003.

[87] Hill, M.L.; Kim, Y.S.; Einsla, B.R.; Harrison, W.L.; Wang, F.; Hickner, M.A.; McGrath, J.E. Zirconium Hydrogen Phosphate/Disulfonated Poly(arylene ether sulfone) Copolymer Composite Membranes for Proton Exchange Membrane Fuel Cells. *J. Membr. Sci.* **2005**, *in progress.*

[88] Yang, C.; Srinivasan, S.; Bocarsly, A.B.; Tulyani, S.; Benziger, J.B. A Comparison of Physical Properties and Fuel Cell Performance of Nafion and Zirconium Phosphate/Nafion Composite Membranes. *J. Membr. Sci.* **2004**, *237*, 145-161.

2.2. Five-Membered Ring Polyimides

Polyimides are polymers that have heterocyclic imide functionalities in their repeat unit. They are generally synthesized from the reaction of diamines with dianhydrides. Due to their wide utility in a number of applications, a broad range of synthetic routes have been developed in an attempt to facilitate easier and more cost-efficient methods of preparation.



R = cycloaliphatic or aromatic

R′ = aliphatic or aromatic

Figure 2-17. General structure of polyimides

This review of polyimides will be divided into two main sections, five-membered ring polyimides and six-membered ring polyimides (or polynaphthalimides). Five-membered ring polyimides will be discussed first, due to the fact that they are the more common of the two, although six-membered ring polyimides will receive greater attention as they are the main focus of this research.

2.2.1. Synthetic Routes

2.2.1.1. Classical Two-Step Route

The two-step route to synthesize polyimides involves an intermediate, a poly(amic acid). This method was pioneered by DuPont and is used to synthesize high molecular weight insoluble polyimides, such as Kapton®.

In the first stage of a two-step aromatic polyimide synthesis, a dianhydride and an aromatic diamine are dissolved in a dipolar aprotic solvent, such as N-methylpyrrolidinone (NMP), dimethylacetamide (DMAc), or dimethylsulfoxide (DMSO). The strong hydrogen bonding interactions between the poly(amic acid) and the solvent drives the equilibrium to poly(amic acid). This reaction is favored when a more basic aprotic solvent is used due to its favorable interaction with the strong acid formed in the reaction. The formation of the poly(amic acid) is not carried out at higher than ambient temperatures due to the exothermic nature of the reaction.[89] In fact, higher molecular weight poly(amic acids) are obtained at lower temperatures.[90] The formation of high molecular weight poly(amic acid) is complete within 24 hours or less, and at this point the soluble polymer can be cast into a film. The poly(amic acid) is then cyclodehydrated using either a thermal or a chemical process to form the final polyimide.

Although the major reaction is poly(amic acid) formation, some side reactions may also occur. Small amounts of dianhydride may hydrolyze in the presence of water. Water may be produced as a by-product of the imidization or as an impurity in the

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[89] Harris, F. W.; Wilson, D.; Stenzenberger, H. D.; Hergenrother, P. M., Eds. Polyimides, Blackie & Son Ltd.:Glasgow and London, 1990.

[90] Sroog, C.E.; Endrey, A.L.; Abramo, S.V.; Berr, C.E.; Edwards, W.M.; Olivier, K.L. Aromatic Polypyromellitimides from Aromatic Polyamic Acids. *J. Polym. Sci.: Part A: Gen. Papers* **1965**, *3*, 1373-1390.

reaction medium. Hydrolysis will shift the equilibrium balance of the anhydride and the amine endgroups. As a result, the *o*-dicarboxylic acid that is formed is unreactive with aromatic diamines under the conditions of the poly(amic acid) reaction and the molecular weight is limited. For this reason, it is imperative that the monomers and solvent are free of water. This means carefully drying monomers and distilling solvents before polymerization.

The reaction to form a poly(amic acid) is thought to begin with the formation of a charge transfer complex between the anhydride and diamine. The amine attacks the carbonyl carbon, displacing the adjacent carboxyl group, which is stabilized by hydrogen bonding with the polar aprotic solvent, pushing the reaction toward completion of the polymerization. Using this approach, high molecular weight poly(amic acid)s can be synthesized from a wide variety of dianhydrides and diamines. Given long enough reaction times, even relatively unreactive monomers can be used to produce high molecular weight polyimides.

Since the propagation of the poly(amic acid) proceeds after a nucleophilic substitution reaction at the carbonyl carbon of the anhydride, anhydrides that are more electrophilic tend to react faster. Dianhydride reactivity, the ability to accept an incoming electron pair from a nucleophile, is correlated with the electron affinity (E_a) of the dianhydride.[89] Hence, the dianhydride with the greatest elecrophilicity will react first with a given nucleophile. Additionally, diamine reactivity has been correlated to basicity, or pK_a. More basic diamines, such as *p*-phenylenediamine (*p*-PDA) and 4,4'-oxydianiline (ODA), tend to have higher reaction rates.

2.2.1.2. Bulk Imidization

Polyamic acids, which may precipitate upon cyclization due to the increase in chain rigidity, are generally cast from solution and thermally imidized in a film form, which is also known as bulk imidization. A film of poly(amic acid) is cast onto a substrate, often a glass plate, and is heated in stages in a vacuum oven or inert atmosphere to induce cyclization and remove the solvent and water condensate that is produced during imidization. A widely employed thermal cycle conducted under vacuum or nitrogen to remove water and prepare bubble-free films is as follows: 30 ^{o}C for one hour, 100 ^{o}C for one hour, 200 ^{o}C for one hour, and 300 ^{o}C for one hour.[91] The best results are obtained when the final reaction temperature is above the ultimate T_g of the system. This final annealing allows the chains enough freedom of motion to release nearly all the trapped water and solvent. The heating strategy used to convert the poly(amic acid) to the polyimide is significant for the following reasons. The trapped air and water evolved during the cyclodehydration reaction need time to diffuse out of the film. More importantly, the degree of imidization is extremely dependent on the mobility of the chains during this thermal treatment, which is dependent on the concentration of residual solvent, and the type of diamine and dianhydride moiety. The mobility of the chains is believed to be necessary for the nucleophilic substitution reaction between the nitrogen and carbonyl acid. However, because the viscosity of these poly(amic acid) solutions increases with decreasing solvent, residual solvent is necessary for the plasticization that facilitates film formation, and gives the necessary chain mobility needed to obtain high degrees of imidization.

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[91] Snyder, R.W.; Thomson, B.; Bartges, B.; Czerniwski, D.; Painter, P.C. FTIR Studies of Polyimides: Thermal Curing. *Macromolecules*, **1989**, *22*, 4166-4172.

2.2.1.3. Chemical Imidization

The primary disadvantage of thermal imidization is that a decrease in molecular weight, which has a detrimental effect on the mechanical properties of the resulting polyimide, is often observed. To avoid this effect and to obtain polyimides of similar molecular weight to their corresponding poly(amic acid), it is necessary to employ milder conditions for cyclodehydration. Chemical imidization is one method of choice, and is accomplished using chemical agents as catalysts for ring closure at temperatures below those of thermal imidization, typically at room temperature. The most commonly used dehydrating reagents are acid anhydrides, such as acetic, propionic, *n*-butyric, benzoic anhydrides, etc. in aprotic polar solvents or in the presence of tertiary amines. Commonly used amine catalysts include trialkylamines, pyridine, lutidine, and N-methylmorpholine.[92] Various combinations of chemical reagents have been used, although the most widely used to produce polyimides is an equimolar mixture of pyridine and acetic anhydride.[93] The mechanism of formation involves a mixed anhydride intermediate followed by an iminolactone and then the imide linkage, which is the thermodynamically favored product.

Poly(amic acid)s can also be converted to their corresponding polyisoimide with a number of other chemical reagents. For instance, a combination of pyridine and trifluoroacetic anhydride favors isoimide formation. Although isoimide linkages are unstable due to their decreased thermal stability and mechanical properties, with respect to imide moieties, polyisoimides have found commercial applications most likely due to

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[92] Angelo, R. J.; Golike, R. C.; Tatum, W. E.; Kreuz, J. A., Eds. Recent Advances in Polyimide Science and Technology; Society of Plastic Engineers: Poughkeepsie, New York, 1987; p.67.

[93] Roderick, W.R. The “Isomerism” of N-Substituted Maleimides. *J. Am. Chem. Soc.* **1957**, *79*, 1710-1712.

their improved processability arising from a lower glass transition temperature, T_g, and increased solubility.[14] Additionally, isoimides can be thermally converted to imides in the presence of a tertiary amine.

2.2.1.4. Solution Imidization

A well known example of a commercial polyimide prepared by a one-pot solution method is General Electric's Ultem^{TM}, obtained by reacting diamines and dianhydrides in *o*-dichlorobenzene (*o*-DCB). The reaction is shown below in Figure 2-18.

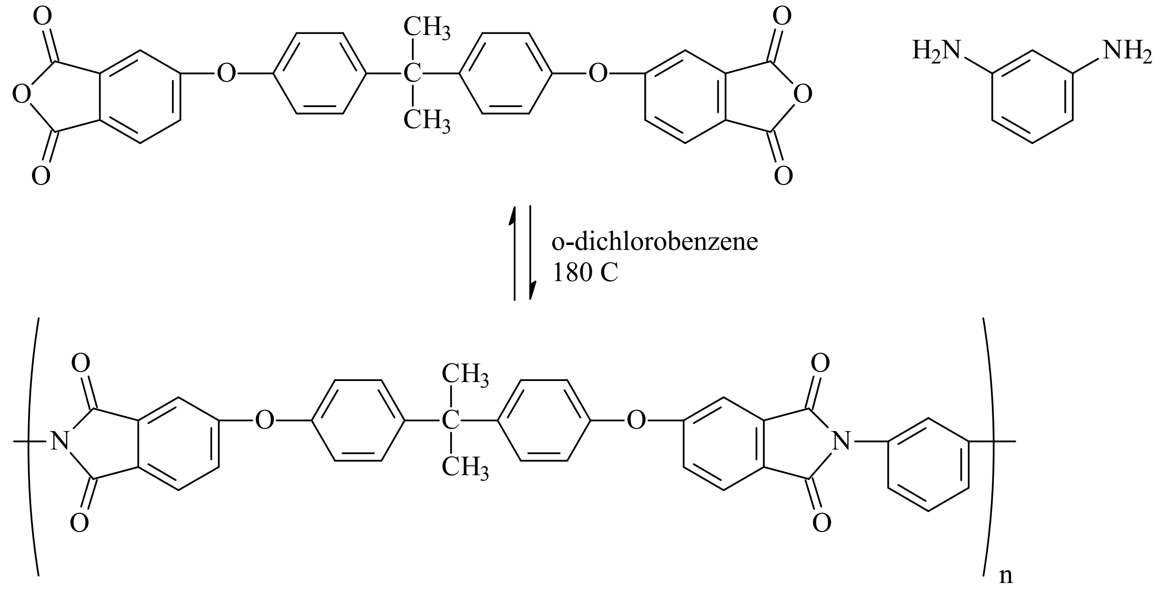

Figure 2-18. Synthesis of Ultem^{TM} polyimide by one-step solution polymerization

To prepare soluble, fully cyclized polyimides containing aryl groups, the rigid-rod structure must be modified to reduce stiffness and interchain ordering. Several strategies have been developed to make soluble amorphous polyimides without sacrificing the excellent physical properties, which are outlined below:[94,95]

- Incorporate flexible bridging units, such as -O- , -S- , -CO- , $-SO_2-$, $-C(CH_3)_2-$, $- C(CF_3)_2-$
- Introduce monomers with bulky side groups
- Incorporate monomers containing meta linkages
- Introduce asymmetrical and cardo (loop) structures along the backbone
- Control molecular weight and endcap with mono-functional groups

The advantages of using one or several of these strategies to produce soluble amorphous polyimides are as follows:

- One-Step Reaction: homogeneous solution imidization
- Fewer than 1% of the amic-acid groups remain unimidized
- Long shelf life due to hydrolytic stability of the polyimide
- The resulting polyimide is soluble in polar solvents for spin casting or solution casting films
- No release of water during film drying
- Isotropic physical properties

Polyimides which remain soluble in the fully cyclized form can be thermally imidized from the corresponding poly(amic acid) in solution at elevated temperatures.

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[94] Huang, S.J.; Hoyt, A.E. The Synthesis of Soluble Polyimides. *Trends in Polym. Sci.* **1995**, *3(8)*, 262-271.

[95] Sato, M. Polyimides; In Plast. Eng.: Handbook of Thermoplastics, V. 41; Marcel Dekker: 1997.

Cyclodehydrations are fulfilled in high boiling point solvent at 160 – 200 °C in the presence of an azeotropic solvent.[96] Azeotroping solvents are typically used to remove the water formed during the reaction and drive the reaction to completion. The solvent of choice needs to be capable of transporting the water from the reaction. Typical azeotroping solvents are toluene, xylene, *o*-DCB, or cyclohexylpyrrolidone (CHP). In contrast to bulk polymerization, this process can be performed at much lower temperatures. Therefore, degradation and other side reactions may be prevented.

It was demonstrated that the poly(amic acid) chains cleaved to form *o*-dicarboxylic acids and amine endgroups as water liberated from the reaction caused initial hydrolysis of partially imidized poly(amic acid)s.[97] As the reaction proceeded, the endgroups recombined and intrinsic viscosity increased to form high molecular weight polyimides. This process can be followed by ^{1}H NMR by monitoring the concentration of free amine in solution. Kim et al. found that the rate determining step is acid catalyzed and second-order.[98,99] This phenomenon occurs in bulk thermal imidization. Preparation of high molecular weight poly(amic acid)s is not necessary in this procedure. Although imidization still proceeds via an amic acid intermediate, the concentration of amic acid is very low during the polymerization because of its short lifetime at high temperature due to rapid imidization, or conversion to amine and anhydride. Polyimides may also be

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[96] McGrath, J. E.; Rogers, M. E.; Arnold, C. A.; Kim, Y. J.; Hedrick, J. C. Synthesis and Blend Behavior of High Performance Homo- and Segmented Thermoplastic Polyimides. *Makromol. Chem., Macromol. Symp.* **1991**, *51*, 103-125.

[97] Hodgkin, J. H. Reactivity Changes During Polyimide Formation. *J. Polym. Sci., Polym. Chem. Ed.* **1976**, *14*, 409-431.

[98] Kim, Y.J. Kinetic and Mechanistic Investigations of Polyimide Formation and Characterization of Their Blends with Polybenzimidazoles. Ph.D. Dissertation, Virginia Tech, Blacksburg, VA, 1992.

[99] Kim, Y.J.; Glass, T.E.; Lyle, G.D.; McGrath, J.E. Kinetic and Mechanistic Investigations of the Formation of Polyimides Under Homogeneous Conditions. *Macromolecules* **1993**, *26*, 1344-1358.

prepared in one pot. After the formation of poly(amic acid)s, they can be directly imidized in solvent at high temperature.

2.2.1.5. Ester-Acid Route

In an effort to alleviate dianhydride water sensitivity and subsequent hydrolysis, NASA developed a novel method to synthesize polyimides from ester-acids. The diester diacid dianhydride derivatives can be synthesized from dianhydrides in alcohol in the presence of a tertiary amine catalyst. Additionally, the diester-diacid is generally more soluble than the parent dianhydride. The ester-acids formed can be prepared in the presence of commercially available solvents and are very tolerant of water content in both the solvents and reactor. Among the proposed polymerization mechanisms are: 1) the initial formation of a salt in a fashion similar to commercial nylon synthesis, followed by amidization and imidization; 2) attack of the amine on the esters, yielding an intermediate amic acid prior to imidization; and 3) in situ reformation of the dianhydride from the diester diacid followed by polymerization of dianhydride and diamine. Although it is claimed in the patent literature that salt formation occurs when aliphatic diamines are used, it is doubtful that that this occurs with aromatic diamines due to their comparatively low basicity. Sillion and coworkers observed amic acid at temperatures of up to 160 °C. during the synthesis of polyamides from ester acids in NMP.[100] This observation has contributed to the view that the polymerization begins with the amine ester reaction and is followed by imidization of the amic acid intermediate, although there is evidence that contradicts this view.

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[100] Quenneson, M. E.; Garapon, J.; Bartholin, M.; Sillion, B. In *Proceedings of the Second International Conference on Polyimides:* Ellenville, New York, 1985; p 74.

The factors necessary for the consistent synthesis of soluble polyimides by the ester acid method have been investigated.[101] Diester diacids are easily prepared by dissolving highly purified dianhydride in refluxing ethanol. The addition of a catalyst that can accept protons greatly accelerates the rate of formation. Traditionally, a small amount of triethylamine is used as a catalyst. Moy showed that at higher temperatures (100 – 150 ^{o}C) the anhydride functionality is reformed from the ester-acid. It was also shown that nucleophilic attack on the ester carbonyl by the diamine did not occur, but instead the ester-acid reverts to the anhydride at elevated temperatures (>140 ^{o}C). In so doing, the dianhydride becomes reactive toward amines. These studies generated a set of reaction conditions that included solids contents of 15 to 20 weight percent (w/v) in NMP and temperatures of 170 – 180 ^{o}C for a period of not more than 24 hours that allowed the synthesis of high molecular weight as well as controlled molecular weight polyimides. This process has the advantage of being a "one-pot" reaction.

2.2.2. Polyimide Properties

Aromatic polyimides are extensively used in microelectronics and aerospace industries for their excellent mechanical properties, and may possess low dielectric constants, thermal stability, chemical resistance, and high glass transition temperatures. Polyimides are reaction products of diamines and dianhydrides, and the final properties such as tensile strength, toughness, modulus, and upper-use temperature depend on the selection of the starting monomers. These aromatic-based polyimide materials generally display high glass transition temperatures in the range of 200 to 400 ^{o}C or higher, which

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[101] Moy, T.M. Synthesis and Characterization of Soluble, High Temperature Polyimides. Ph.D. Dissertation, Virginia Tech, Blacksburg, VA, 1993.

greatly depend on the stiffness of the backbone chain. In addition, fully imidized aromatic polyimides, due to their highly conjugated, rigid-rod-like chemical structures, are insoluble in most organic solvents. Consequently, direct processing of polyimides becomes impossible in their imidized forms.

Of the various alternatives to design novel processable polyimides, some general approaches have been universally adopted: introduction of aliphatic or another kind of flexible segment, which reduces chain stiffness;[102,103] introduction of bulky side chain substituents,[104,105] which help in the separation of polymer chains and hinder molecular packing and crystallization; use of enlarged monomers containing angular bonds, which suppress coplanar structures;[106] use of 1,3-substituted instead of 1,4-substituted monomers, and/or asymmetric monomers that lower regularity and molecular ordering; and preparation of co-polyimides from two or more dianhydrides or diamines. However, factors leading to better solubility or lower T_g or melting temperatures, T_m, in a polymer often conflict with other important requirements, such as mechanical properties, thermal resistance or chemical resistance. Therefore, an adjusted degree of modification should be applied to optimize the balance of properties.

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[102] Sroog, C.E. Introduction of Aliphatic Groups into Polyimides. *J. Polym. Sci Part.C.* **1967**, *16*, 1191-1198.

[103] Imai, Y.; Maldar, N.N.; Kakimoto, M. Synthesis and Characterization of Soluble Polyimides from 2,5-Bis(4-Aminophynyl)-3,4-Phenylthiophene and Aromatic Tetracarboxylic Dianhydrides. *J. Polym. Sci.: Part A: Polym. Chem.* **1984**, *22*, 2189-2196.

[104] Keller, U.; Eiselt, P.; Schmidt, H.-W. Synthesis and Thermal Properties of Aryl-Substituted Rod-Like Polyimides. *J. Polym. Sci.: Part A: Polym. Chem.* **1993**, *31*, 141-151.

[105] Lozano, A.E.; de la Campa, J.G.; de Abajo, J.; Preston, J. Novel Polyimides. *J. Polym. Sci.: Part A: Polym. Chem.* **1994**, *35*, 873-880.

[106] Kaneda, T.; Katsura, T.; Nakagawa, K.; Makino, H. High-Strength-High-Modulus Polyimide Fibers II. Spinning and Properties of Fibers. *J. Appl. Polym. Sci.* **1986**, *32*, 3151-3176.

2.3. Six-Membered Ring Polyimides (Polynaphthalimides)

Amorphous polyimides derived from aromatic diamines and phthalic dianhydrides display relatively low chemical and hydrolytic stability. This effect is principally attributed to the strained five-membered imide moieties in the formed heterocycles, large positive charges on the carbonylic carbons in the systems, and comparatively low orders of the bonds C-C(O) and N-C(O). Far lower ring strain, positive charges on the carbonylic carbon atoms and higher orders of the corresponding bonds are characteristic of six-membered ring polyimides, or polynaphthalimides. In general, this points to a possible enhancement in thermal and chemical stability of polyimides by replacing the bis(phthalic anhydrides) with bis(naphthalenic) dianhydrides. Previous work has shown that polynaphthalimides and polynaphthaloylenebenzimidazoles, which utilize bis(naphthalenic anhydrides) as the monomers, display superior chemical, thermal and fire resistance compared with the analogous five-membered ring systems.[107]

2.3.1. Commercially Available Naphthalenic Dianhydrides

Due to their commercial availability, naphthalene-1,4,5,8-tetracarboxylic dianhydride (NDA) and perylene-3,4,9,10-tetracarboxylic dianhydride (PDA) have become attractive six-membered ring dianhydrides for the preparation of polynaphthalimides. Polyimides synthesized from either NDA or PDA and commercially available diamines such as m-phenylenediamine, *p*-phenylenediamine, and 4,4’-oxydianiline are insoluble in many organic solvents. More flexible diamines or

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[107] Rusanov, A.L. Novel Bis(Naphthalic Anhydrides) and Their Polyheteroarylenes with Improved Processability. *Adv. Polym. Sci.* **1994**, *111*, 115-175.

copolymers from two or more different diamines must be used to improve the solubility of six-membered ring polyimides.

2.3.1.1. Naphthalene-1,4,5,8-tetracarboxylic dianhydride (NDA)

Polymers prepared from NDA and aromatic diamines have been extensively studied.[108,109,110] To date, NDA is essentially the only six-membered ring dianhydride that has been used for the synthesis of proton exchange membranes, probably due to its relatively low cost, high reactivity, and availability. Rusanov *et al.* have shown through electronic calculations that NDA is the most reactive of the naphthalenic dianhydrides, although a more recent paper shows otherwise.[114] A novel dianhydride, which will be discussed later, includes carbonyl moieties and yields polymers with higher intrinsic viscosities. Hodgkin discussed the reactivity of NDA with several aromatic diamines. When an amine reacts with NDA, the dianhydride becomes more reactive towards another amine. Therefore, when NDA reacts with aniline, the major product is the disubstituted molecule (Figure 2-19).

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[108] Choi, D.-S.; Chong, Y.S.; Whitehead, D.; Shimizu, K.D. Molecules with Shape Memory Based on Restricted Rotation. *Org. Lett.* **2001**, *3*, 3757-3760.

[109] Hodgkin, J.H. Reactivity Changes During Polyimide Formation. *J. Polym. Sci.: Polym. Chem. Ed.* **1976**, *14*, 409-413.

[110] Ronova, I.A.; Ponomarev, I.I.; Kovalevsky, A.Y.; Shishkin, O.V. Molecular Design of Rigid-Chain Polyheteroarylenes and the Effect of Substituents at the Central Heterocyclic Fragment on the Polyheteroarylene Equilibrium Rigidity. *High Perform. Polym.* **1999**, *11*, 355-365.

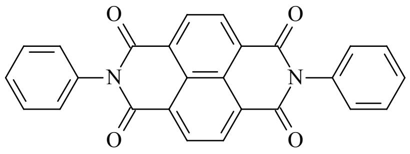

Figure 2-19. Reaction product of NDA with aniline

Moreover, when NDA is placed in solution with an aromatic diamine at temperatures higher than 80 ^{o}C, the disubstituted diimide is again the main product. A representative molecule of the reaction between ODA and NDA is shown in Figure 2-20. This example illustrates that the reactivity of the second amine group is drastically decreased after the first amine reacts with the dianhydride.

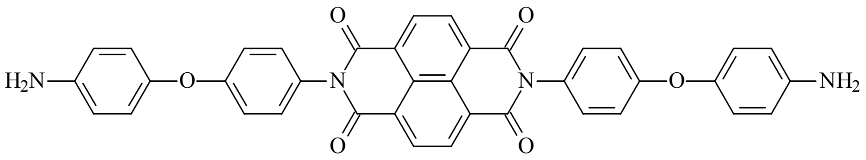

Figure 2-20. Reaction product of NDA with 4,4'-oxydianiline

2.3.1.2. Perylene-3,4,9,10-tetracarboxylic dianhydride (PDA)

Large π-conjugated systems are widely used as chromophores in dye-stuff chemistry. A particularly important class of these compounds is perylene and its derivatives. Due to their high thermal and photochemical stability, perylene derivatives are key components in solar cells, fluorescent solar collectors, and in the development of new lasers.[111] Several series of polyimides were synthesized using PDA and derivatives

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[111] Hiramoto, M.; Kishigami, Y.; Yokoyama, M. Doping Effect on the Two-Layer Organic Solar Cell. *Chem. Lett.* **1990**, *1*, 119-122.

of PDA, including 1,6,7,12-tetrachloro-3,4,9,10-perylene dianhydride (Cl-PDA).[112,113] Using the four chlorine groups on Cl-PDA, Mullen and coworkers were able to synthesize six-membered ring polyimides containing sulfonic acid groups. Cl-PDA was reacted with phenol through a nucleophilic aromatic substitution reaction. The resulting monomer was then polymerized with a diamine and finally sulfonated with concentrated sulfuric acid at room temperature. The sulfonation occurred on the pendent phenyl rings due to the electron donating ability of the ether linkage. No evidence of side reactions (e.g., three-fold sulfonation instead of four-fold sulfonation or cleavage of the phenoxy substituents) was detected by ^{1}H NMR. The authors state that this sulfonated polymer forms good films upon solution casting and is soluble in water. However, they do not suggest any applications or properties other than improved solubility.

2.3.2. Novel Dianhydrides

As with five-membered ring dianhydrides, introducing flexibile “hinge” bonds or bulky substituents in the naphthalenic dianhydride will improve the solubility of the resulting polyimides. The most straightforward way to improve the solubility of six-membered ring polyimides is to introduce single bonds or "hinge" groups between the two naphthalenic anhydrides. Several dianhydrides have been synthesized using ether, sulfide, sulfone, ketone, or methyl groups as the link between the naphthalenic anhydrides (Figure 2-21).

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[112] Dotcheva, D.; Klapper, M.; Mullen, K. Soluble Polyimides Containing Perylene Units. *Macromol. Chem. Phys.* **1994**, *195*, 1905-1911.

[113] Quante, H.; Schichting, P.; Rohr, U.; Geerts, Y.; Mullen, K. Novel Perylene-Containing Polymers. *Macromol. Chem. Phys.* **1996**, *197*, 4029-4044.

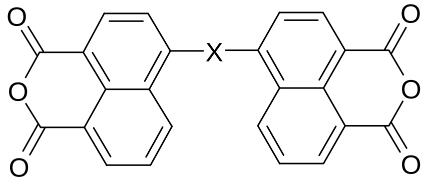

Figure 2-21. Structure of novel dianhydrides where X = bond, O, S, SO_2, CO, or CH_2

Polyimides derived from ODA and the above dianhydrides were synthesized in *m*-cresol. All were soluble in *m*-cresol at 10% concentration, whereas polyimides from NDA and ODA precipitate from *m*-cresol during the polymerization. By introducing these electron-donating substituents into bis(naphthalenic anhydride)s, their electrophilic reactivity decreases and consequently reductions in molecular weight (intrinsic viscosity) were noticed.

Six-membered ring polyimides have also been prepared from dianhydrides containing ester or amide linkages.[107] Although this improves the solubility of the resulting polymer, it also reduces the primary advantage of these systems, which is chemical stability.

Of particular interest are the dianhydrides shown in Figure 2-22, because the carbonyl groups increase the reactivity of the dianhydride with aromatic diamines.[114,115,116] The resulting polymers have higher molecular weight and improved

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[114] Sek, D.; Pijet, P.; Wanic, A. Investigation of Polyimides Containing Naphthalene Units: 1. Monomer Structure and Reaction Conditions. *Polymer* **1992**, *33*, 190-193.

[115] Rusanov, A.L.; Bulycheva, E.G.; Bocharov, S.S. Thermally Stable Polymers Based on Bis-Acenaphthyls. *J. Thermal Anal.* **1990**, *36*, 1685-1698.

[116] A.L. Rusanov and E.G. Bulycheva. "New Bis(naphthalic anhydride) and Polyheteroarylenes on their Base," in Polyimides and Other High-Temperature Polymers, M.J.M. Abadi and B. Sillion, Eds., Elsevier: Amsterdam, 1991.

solubility, with respect to NDA and PDA. Several groups have synthesized these monomers from acenaphthene and aromatic dicarboxylic acid dichlorides via a Friedel-Crafts reaction. Rusanov *et al.* studied the conditions of the synthesis in detail. It was concluded that the yield and purity are dependent on catalyst nature and quantity, solvent, reagent mixing order, temperature and reaction duration. The optimal conditions for the condensation reactions are reaction times of four hours at 0 to 60 ^{o}C, with tetrachloroethane as the solvent, and aluminum chloride as the catalyst. Bis(naphthalenic anhydride)s were prepared via the oxidation of bis-acenaphthyls and dehydration of the tetracarboxylic acids. These bis(naphthalenic anhydrides) were subsequently used for the preparation of poly(naphthalimide)s.

The effect of polyimide structure on the reduced viscosity was studied. The authors used several different aromatic diamines and two naphthalic dianhydrides, 1,3- and 1,4-bis(1,8-dicarboxylic anhydride-4-naphthaloyl)benzene.

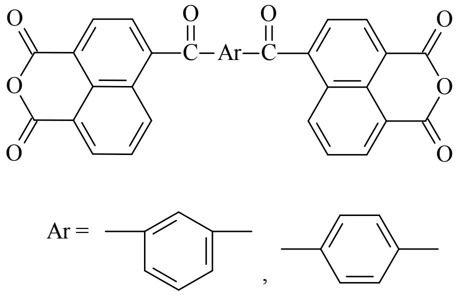

Figure 2-22. Structure of novel dianhydrides incorporating ketone linkages

Both the diamine and dianhydride structure have an effect on the reduced viscosity. The polyimides derived from 1,4-bis(1,8-dicarboxylic anhydride-4-

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naphthaloyl)benzene display higher reduced viscosities than those derived from 1,3-bis(1,8-dicarboxylic anhydride-4-naphthaloyl)benzene when the same diamine was used. This result demonstrates that para-linkages in the dianhydride produce higher molecular weight materials than meta-linkages. This conclusion is also true for the diamines. Polyimides prepared from 1,4-phenylenediamine display higher reduced viscosities than those prepared from 1,3-phenylenediamine with the same dianhydride.

2.3.3. Reaction Conditions and Mechanism of Six-Membered Ring Polyimide Formation

The stability of six-membered ring anhydrides leads to enhanced chemical and thermal stability for the resulting polyimides. However, the reactivity of the naphthalenic anhydride is much lower than its phthalic counterpart. Thus, preliminary attempts to obtain high molecular weight polynaphthalimides were unsuccessful. Only a few research groups have successfully synthesized high molecular weight six-membered ring polyimides, therefore an in-depth study of the reaction conditions and mechanism of naphthalimide formation will be considered in this section.

Six-membered ring anhydrides are more stable and their reactivity towards an amine group is lower than that of their five-membered analogues. Therefore it is necessary to utilize catalysts in the reaction of such dianhydrides with diamines. Several catalysts have been used, including benzoic acid, isoquinoline, imidazole, quinoline, pyridine, triphenylphosphine, and triphenyl phosphine oxide. Specifically, the effect of catalyst type, catalyst concentration, mixing catalysts, and addition time of each catalyst on the reduced viscosity of the resulting polyimides was studied. Phosphorus containing catalysts have little or no effect on the reduced viscosity, whereas acidic and basic catalysts have significant effects. The most effective catalyst system was a 2:1 molar ratio of benzoic acid to dianhydride added at the beginning of the reaction, with isoquinoline added after nine hours. Here, the number of moles of isoquinoline added is equal to the moles of benzoic acid. Furthermore, when using only one catalyst, benzoic acid yields the highest molecular weight polymers. As a result of these findings, several groups have used benzoic acid or benzoic acid/isoquinoline as catalysts in six-membered ring polyimide polymerization.[117]

A series of model compounds from 4-benzoyl-1,8-naphthalene anhydride and aromatic amines and diamines were synthesized and several techniques including ^{13}C and ^{15}N NMR were used to study the mechanism of the one-step high temperature polycondensation of six-membered ring polyimides.[118] It is thought that this mechanism is similar to the polycondensation of phthalic imides, where the intermediate is a poly(amic acid). In a one-step high temperature polycondensation of five-membered dianhydrides and diamines, the poly(amic acid) is formed first and this species quickly dehydrates to form the polyimide. The poly(amic acid) is supposed to be a short-lived intermediate, although it has not been detected.

To determine the role of the acidic catalyst (benzoic acid) in the polymerization, reactions of 4-benzoyl-1,8-naphthalene anhydride and several amines (ODA, 4-biphenylamine, 4-phenyloxyaniline) were conducted out at several levels of acidity.

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[117] Sek, D.; Wanic, A.; Schab-Balcerzak, E. Novel Approach to the Mechanism of the High-Temperature Formation of Naphthalimides. *Polymer* **1993**, *34*, 2440-2442.

[118] Sek, D.; Wanic, A.; Schab-Balcerzak, E. Investigation of Polyimides Containing Naphthalene Units. II. Model Compound Synthesis. *J. Polym. Sci.: Part A: Polym. Chem.* **1995**, *33*, 547-554.

Ideally, the acid should catalyze the formation of the amic acid and produce higher yields of the model compound. However, as the acidity of the solvent increased, the yield decreased. This finding suggests that the poly(amic acid) is not an intermediate of the reaction, and NMR confirms this phenomenon.

For model compounds synthesized at different levels of acidity, ^{13}C NMR spectra showed that the structures were independent of reaction conditions. To determine whether the model compounds were imides or isoimides, the carbon positions for an isocyanate (isoimide) and a tertiary amine (imide) were determined. In all cases, the observed values are closest to the isoimide chemical shifts.

The nitrogen atoms in the imide and isoimide structures have sp^3 and sp^2 hybridization, respectively. Therefore, ^{15}N NMR spectra were also obtained for the model compounds and a single peak was observed at –197.432 ppm. Another model compound was synthesized having sp^2 hybridization. The ^{15}N NMR of this compound showed a peak at the same position. To confirm that different hybridizations of nitrogen have different chemical shifts, a third model compound having sp^2 and sp^3 hybridized nitrogen was synthesized from 4-benzoyl-1,8-naphthalene anhydride and *o*-phenylene diamine for comparison. It displayed two signals at –135.492 ppm and –197.597 ppm, which proves that the original model compounds from 4-benzoyl-1,8-naphthalene anhydride and several amines have the isoimide structure.

Additional methods of characterization, such as mass spectroscopy, ultraviolet-visible spectroscopy (UV-VIS), and differential scanning calorimetry (DSC) were also carried out. These methods confirmed that the intermediate in the one-step high temperature condensation is the isoimide structure.

Model naphthalimide compounds show darker colors when the acidity of the reaction medium increases. Based upon the UV-VIS spectral data, this result suggests that two isomers of the isoimide form in an acidic medium. Imides do not exhibit any absorption above 300 nm. In the UV-VIS spectra of the models synthesized without acid catalyst, absorption bands at 344 nm and 352 nm are present, which correspond to the six-membered lactone carbonyl group and a C=N group, respectively. In the presence of acid, an additional absorption band appears at 480 nm. The UV-VIS spectral data along with DSC analyses suggests that two isomers of the isoimide (*cis* and *trans*) form in the high-temperature polycondensation reaction. The *trans*-isoimide is formed in the presence of an acid, such as benzoic acid, and only the *trans*-isoimide can be converted to the subsequent imide structure. The reaction of aromatic diamines with 1,8-naphthalene type anhydrides under high temperature condensation follow the scheme illustrated in Figure 2-23.

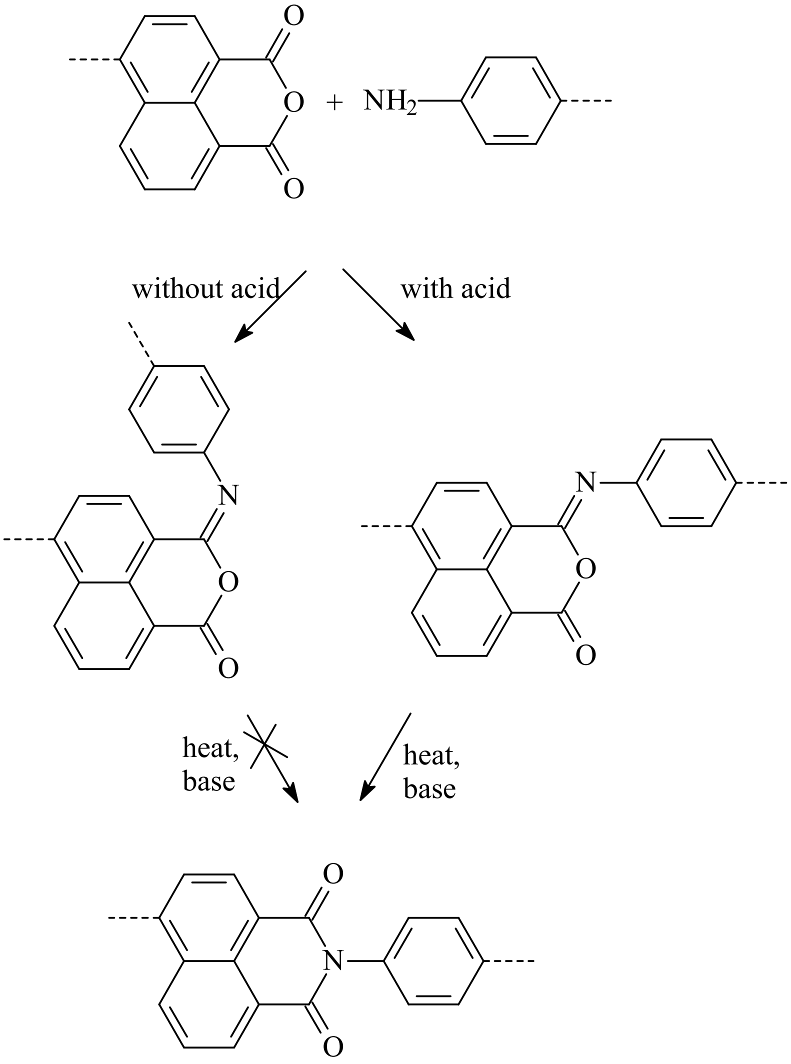

Figure 2-23. Reaction of 1,8-naphthalene type anhydride with an aromatic amine[118]

The only other route to form the *trans*-isomide without a catalyst is to use the hydrochloride form of the diamine in hexamethylphosphorous triamide (HMPT).[119] Analyses of the compounds obtained in *m*-cresol in the presence of benzoic acid and in HMPT using amine hydrochloride as a substrate gave very similar results. HMPT is quite expensive so this route is not a particularly cost effective way of producing polyimides.

Now that a route to six-membered ring polyimide formation has been established, the mechanism of the reaction must be considered. The proposed mechanisms are shown in Figures 2-24 and 2-25.

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[119] Sek, D.; Wanic, A.; Janeczek, H.; Abadie, M.J.M. Investigation of Polyimides Containing Naphthalene Units. IV. Mechanism of Naphthalisoimides Formation and Their Isomerization to Naphthalimides. *J. Polym. Sci.: Part A: Polym. Chem.* **1999**, *37*, 3523-3529.

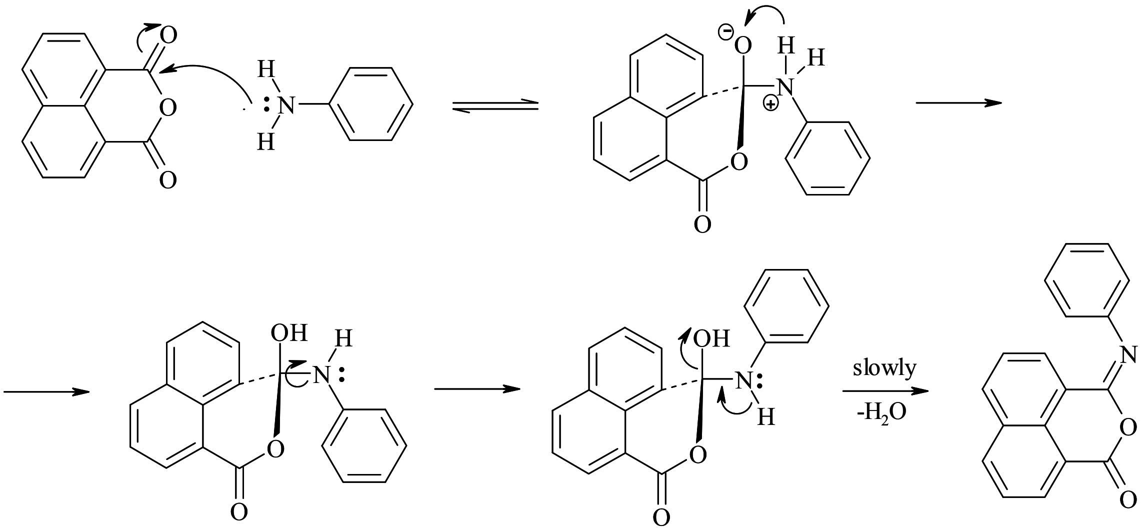

Figure 2-24. Mechanism of *cis*-isoimide formation[119]

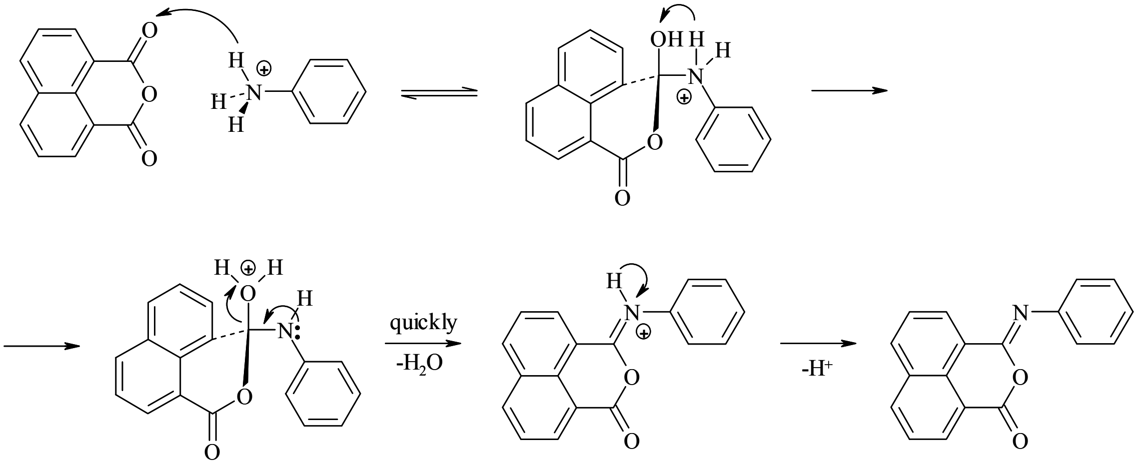

Figure 2-25. Mechanism of *trans*-isoimide formation[119]

2.3.3.2. *Cis*-Isoimide Formation

Nucleophilic attack of the amine at the carbonyl carbon forms an intermediate, as shown in Figure 2-24. Similar to the mechanism in the *trans*-isoimide formation, a proton shift to the carbonyl carbon follows. Proton shifting probably occurs by the mechanism in Figure 2-26. In the next step, water leaves slowly by an E2 elimination. For this to occur, the proton on the nitrogen atom must be in an antiperiplanar position relative to the hydroxyl group. For stereochemical reasons, such methods of elimination favor *cis* isoimide formation.

2.3.3.1. *Trans*-Isoimide Formation

As stated earlier, the *trans*-isoimide is formed either in acidic conditions (benzoic acid) or using the amine hydrochloride (Figure 2-25). Under acidic conditions, the amine is protonated to an ammonium group. After the shift of an ammonium proton to the carbonyl oxygen to form a more electrophilic carbocation, the amine attacks this cation to form (b). The location of both nitrogen protons near the carbonyl oxygen atom is forced by the next step in the reaction and by the interaction of the highly electronegative oxygen. The interaction of these protons with the lactone ether oxygen is also possible, but because the high temperature of the reaction stabilizes the six-membered ring, this pathway through the poly(amic acid) is not possible. Next, one of the protons on the amine group shifts to oxygen to form $-^{+}OH_2$. Water leaves rapidly forming a carbon-nitrogen double bond with the proton on the nitrogen leaving in the final step. For these reasons, the formation of the *trans* structure is favored

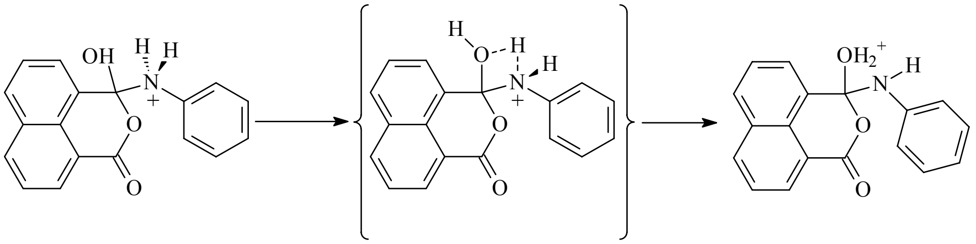

Figure 2-26. Mechanism of direct proton shifting[119]

2.3.3.3. Isomerization of *trans*-Isoimide to Naphthalimide

The isomerization of naphthalisoimides is difficult due to the stability of the six-membered ring. Nonetheless, catalysts can be used to aid this process. Efficient catalysts are high boiling heterocyclic bases, such as quinoline and isoquinoline. Isoquinoline may be more effective due to the position of its nitrogen atom. The mechanism of this reaction proceeds as shown in Figure 2-27. The nitrogen atom on isoquinoline attacks the carbonyl carbon and consequently breaks the carbon-ether oxygen bond. The now nucleophilic nitrogen atom (of what used to be the amine) attacks the carbonyl carbon and isoquinoline leaves forming the naphthalimide.

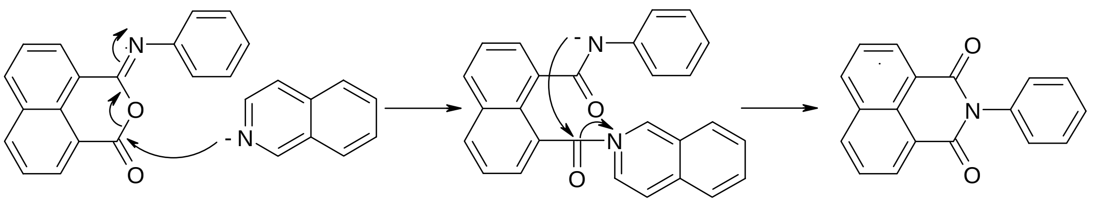

Figure 2-27. Isomerization of naphthalisoimide to naphthalimide in the presence of isoquinoline[119]

2.3.4. Synthesis of Six-Membered Ring Polyimides by Nucleophilic Substitution

Novel approaches to synthesize six-membered ring polyimides include preparation of monomers containing imide moieties followed by use of another polymerization technique. The most common reaction is a nucleophilic substitution reaction between aromatic bisphenolates and dihalides, which is typically used to synthesize poly(arylene ether)s. The primary advantage of this method is that acidic solvents that may be difficult to handle, like *m*-cresol and *m*-chlorophenol, are not used in the polymerization. High molecular weight polymers can be obtained under basic conditions in DMAc or NMP.

Sonpatki *et al.* first prepared aromatic dichloride monomers containing naphthalimide moieties, as shown in Figure 2-28.[120] Since the chlorine atoms in the novel imide monomers are in the para- position to the six-membered imide ring, they are highly susceptible to nucleophilic displacement with oxygen or sulfur reagents. This reactivity allowed the authors to produce high molecular weight polyimides in DMAc. ^{13}C NMR is a good tool to verify the structures of the napthalimide monomers, and to estimate the reactivity of the aromatic chlorine towards nucleophilic substitution. In six-membered ring polyimide synthesis, it is important to know whether the final product has converted to an imide, or if it is the isoimide precursor. Due to the symmetry of the imide structure, it has fewer signals in a ^{13}C NMR than the isoimide structure, and therefore the napthalimide structure can easily be identified. In addition, the reactivity towards nucleophiles increases as the electron density of the carbons bonded to the

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[120] Sonpatki, M.M.; Skaria, S.; Fradet, A.; Ponrathnam, S.; Rajan, C.R.; Synthesis and Structural Study of Poly(thioether-imide-sulfones) Based on 3,3'- and 4,4'-Bis(chloro-1,8-naphthalimido)diphenylsulfone. *Polymer* **1999**, *40*, 4377-4386.

chlorine atoms decrease; as they are the more deshielded carbons. Highly reactive carbons were found to have chemical shifts (δ) greater than 132.5 ppm.[121] The ^{13}C NMR chemical shifts for the two naphthalimide monomers shown below were around 138 ppm.

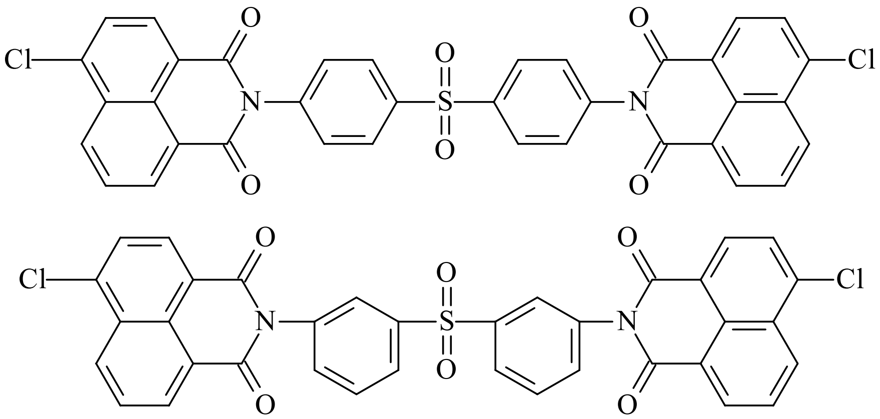

Figure 2-28. Dichloro imide monomers[120]

Sonpatki *et al.* also attempted the nucleophilic polycondensation reactions of the naphthalimide monomers with bisphenols in NMP at 200 °C, but these reactions yielded low molecular weight compounds. The reactions in DMAc, a solvent commonly used for polythioethers and polyether ketones, had high intrinsic viscosities from 0.84 to 1.9 dL/g. Disadvantages to this route are that the monomers are still synthesized in *m*-cresol with large amounts of catalysts.

Zheng and Wang also used a nucleophilic substitution reaction between a naphthalimide containing monomer and a bisphenol to produce high molecular weight

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[121] Nykolyszak, T.; Fradet, A.; Marechal, E. Reactivity of Aryl Chlorides with Sodium Sulfide in the Synthesis of Aromatic Poly(amide thioether)s. *Makromol. Chem. Macromol. Symp.* **1991**, *47*, 363-370.

polymers.[122] The monomer and its synthetic method are shown in Figure 2-29. The inherent viscosities of the polymers synthesized from bis(4-fluorobenzoyl)naphthalimide and several bisphenols were high (up to 1.04 dL/g). Additionally, the six-membered ring polyimides were amorphous and soluble in common organic solvents.

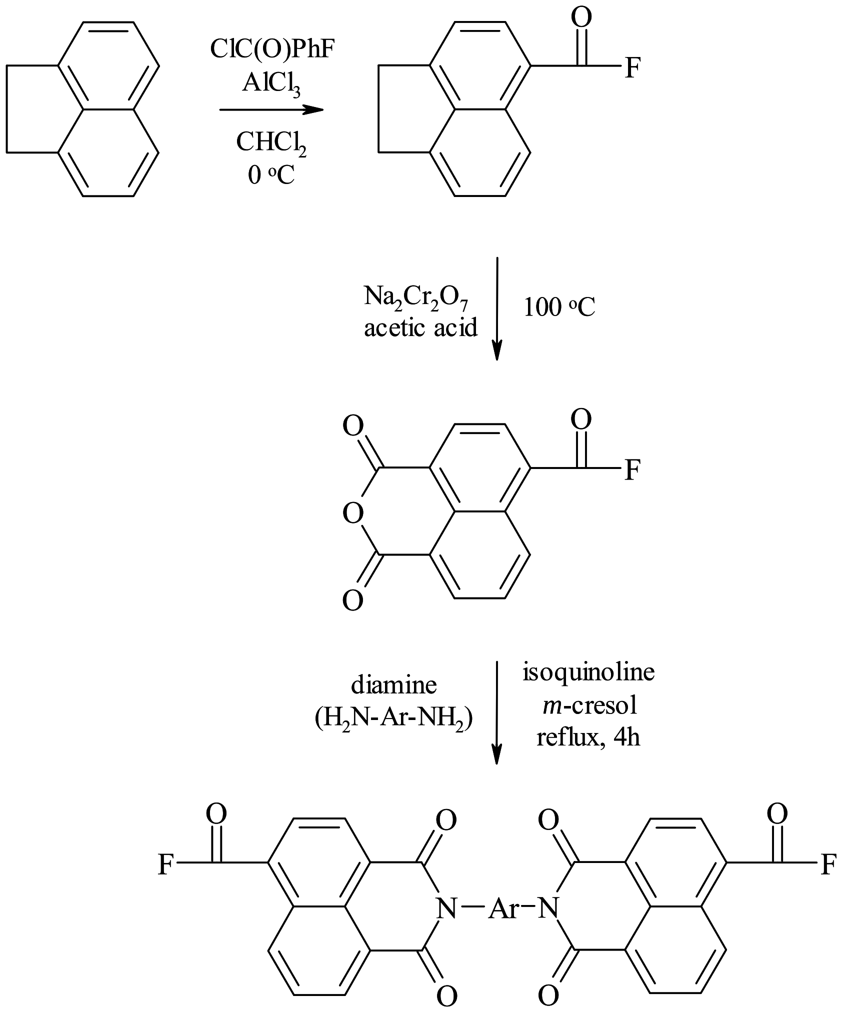

Figure 2-29. Naphthalimide monomer synthesis[122]

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[122] Zheng, H.B.; Wang, Z.Y. Synthesis and Characterization of Poly(ether naphthalimide)s. *J. Polym. Sci.: Part A: Polym. Chem.* **1999**, *37*, 3227-3231.

Several groups have synthesized bisphenols containing naphthalimide moieties.[123,124,125] The approach was to use a commercially available naphthalenic dianhydride, NDA or PDA, and react it with an aminophenol. Then the bisphenols were used to polymerize naphthalimide containing poly(arylene ether)s or polyesters.

Mackinnon and Wang synthesized two novel bisphenols derived from PDA and NDA with 2-(4-aminophenyl)-2-(4-hydroxyphenyl)propane, and polymerized these bisphenols with several aromatic difluorides. The structure and synthesis of the NDA-monomer is shown in Figure 2-30. The intrinsic viscosities of the resulting six-membered ring polyimides are not particularly high (0.11 - 0.44 dL/g), however, the monomer synthesis is particularly interesting. Instead of using *m*-cresol as a solvent and benzoic acid and isoquinoline as the catalysts, the authors synthesized the naphthalimide-containing bisphenols in DMAc or NMP with zinc acetate as a catalyst. They do not state why they chose this route; nevertheless, Mackinnon and Wang obtained pure naphthalimide monomers. Interestingly, Wang previously published a paper which described the synthesis of bis(4-fluorobenzoyl)naphthalimide in *m*-cresol, then published a more recent paper that detailed the naphthalimide synthesis using zinc acetate as the catalyst. Since zinc acetate is considered a Lewis acid, it may act in the same way that benzoic acid does in the *trans*-naphthalisoimide formation.

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[123] Fomine, S.; Fomina, L.; Arreola, R.; Alonso, J.C. Bisimide-Lactamimide Ring Contraction in Six-Membered Polyimides. *Polymer* **1999**, *40*, 2051-2058.

[124] Fomina, L.; Fomine, S.; Pena, P.P.; Ogawa, T.; Alexandrova, L.; Gavino, R. Synthesis and Characterization of Fully Aromatic Lactimimide-Containing Polyesters. *Macromol. Chem. Phys.* **1999**, *200*, 239-245.

[125] Mackinnon, S.M.; Wang, Z.Y. Synthesis and Characterization of Poly(aryl ether imide)s Containing Electroactive Perylene Diimide and Naphthalene Diimide Units. *J. Polym. Sci.: Part A: Polym. Chem.* **2000**, *38(19)*, 3467-3475.

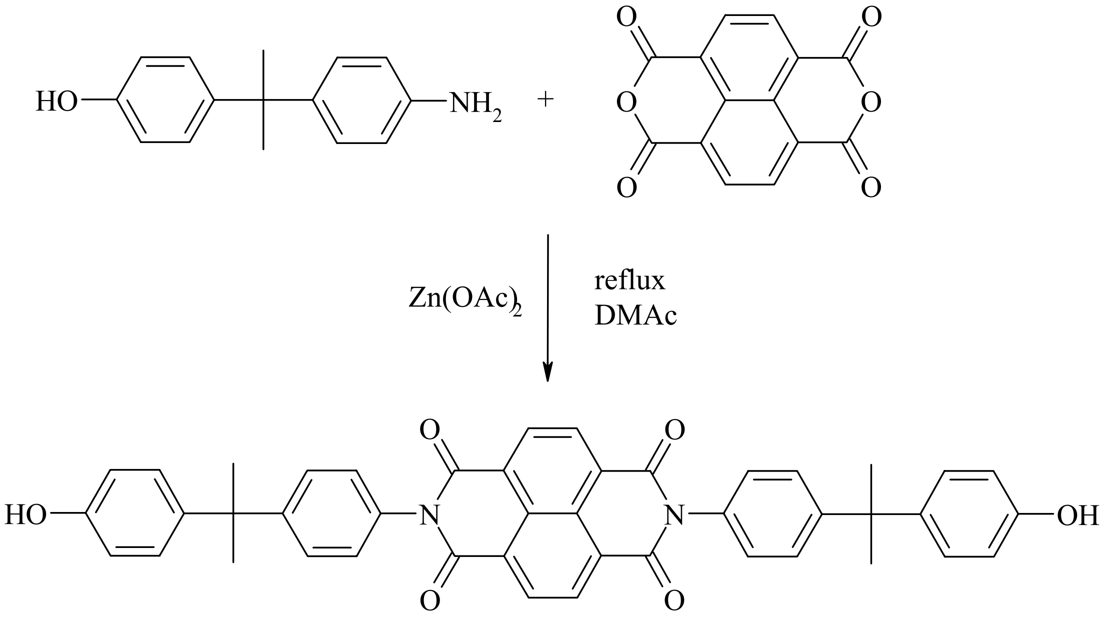

Figure 2-30. Imide-containing bisphenol monomer

Separately, another group published a paper describing the synthesis of novel bisphenols from NDA and either meta- or para-aminophenol.[124,125] To synthesize these monomers, no catalysts were used and 1,4-dioxane was employed as the solvent. The polymers synthesized from these monomers and aromatic dihalides were of medium molecular weight and some were soluble in chloroform.

The advantages of preparing six-membered ring polyimides from a nucleophilic displacement reaction are: (1) the availability of the monomers is good with relatively low cost, and (2) the polymerization conditions are more "friendly". Instead of using the traditional acidic conditions (*m*-cresol, benzoic acid) commonly associated with six-membered ring polyimide synthesis, high molecular weight poly(arylene ether imide)s can be prepared in polar aprotic solvents under basic conditions, ie. poly(arylene ether) synthesis.

Although low molecular weight polymers were obtained, Mackinnon and Wang have described a method to synthesize polynaphthalimides in DMAc with zinc acetate as a catalyst. Additionally, they did not use *m*-cresol in either the monomer or polymer synthesis. This approach is an extremely promising route to the formation of six-membered ring polyimides. Unfortunately, their polyimides were low molecular weight, probably due to their choice of monomers. Sonpatki *et al.* demonstrated that high molecular weight polyimides can be prepared from dichloro-naphthalenic monomers through nucleophilic displacement, because of the increased electrophilicity of the chlorine atom due to the imide moiety. The best route to synthesize high molecular weight polynaphthalimides without using *m*-cresol may be a combination of these techniques. The dichloro-naphthalenic monomers could be synthesized in zinc acetate/DMAc and subsequently used in poly(arylene ether) synthesis with appropriate bisphenols.

CHAPTER 3

SULFONATED NAPHTHALENE DIANHYDRIDE BASED POLYIMIDE COPOLYMERS FOR PROTON EXCHANGE MEMBRANE FUEL CELLS (PEMFC): I. MONOMER AND COPOLYMER SYNTHESIS

Taken From:

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3.1. Abstract

A novel sulfonated diamine, 3,3'-disulfonic acid-bis[4-(3-aminophenoxy)phenyl]sulfone (SA-DADPS), was prepared from *m*-aminophenol and disodium-3,3'-disulfonate-4,4'-dichlorodiphenylsulfone (S-DCDPS). The conditions necessary to synthesize and purify SA-DADPS were investigated in some detail. This sulfonated aromatic diamine containing ether and sulfone linkages was used to prepare N-methylpyrrolidinone soluble, six-membered ring polyimide copolymers containing pendent sulfonic acid groups by a catalyzed one-step high temperature polycondensation in *m*-cresol. High molecular weight film-forming statistical copolymers with controlled

degrees of disulfonation were prepared by varying the stoichiometric ratio of sulfonated diamine (SA-DADPS) in its soluble triethylamine salt form to several nonsulfonated diamines. Three nonsulfonated diamines, bis[4-(3-aminophenoxy)phenyl] sulfone (*m*-BAPS), 4,4'-oxydianiline (ODA), and 1,3-phenylenediamine (*m*-PDA) were utilized to prepare the copolymers. Characterization of the copolymers by ^{1}H NMR, FT-IR, IEC, and TGA demonstrated that SA-DADPS was quantitatively incorporated into the copolymers. Solution-cast films of the sulfonated copolymers were prepared and afforded tough, ductile membranes. Methods were developed to acidify the triethylammonium salt membranes into their disulfonic acid form, which is necessary for proton conduction in a fuel cell. The synthesis and characterization of these materials are described.

3.2. Introduction

Fuel cells are electrochemical devices that convert chemical energy from fuels such as hydrogen or methanol directly into electrical energy. They are environmentally friendly energy sources since, ideally, water and heat are the only byproducts.[126] Proton exchange membrane (PEM) based fuel cell systems are a most promising power source for portable, transportation, and stationary power. These systems produce electric power from two electrochemical reactions: oxidation of hydrogen (or a precursor) at the anode and reduction of oxygen at the cathode. The electric circuit is completed by the transport of protons through the polymeric membrane. Nafion® perfluorinated sulfonic acid copolymers represent the current state-of-the-art PEMs. These membranes have good

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[126] Thomas, S.; Zalbowitz, M. Fuel Cells: Green Power, Los Alamos National Laboratory, Los Alamos, NM, **1999**.

mechanical, thermal and chemical stability along with good conductivity at low temperature (80 °C) and high humidity. Several deficiencies such as high methanol permeability and a major reduction in conductivity at high temperature and low humidity have limited their applicability.[127] As a result, the development of competitive and less expensive PEMs that will overcome these problems is important. Many efforts to synthesize relatively inexpensive and thermally stable alternative membranes, including sulfonated polysulfones[128,129], polybenzimidazoles[130], poly(ether ether ketone)s[131], and polyphenylenes[132] have been initiated and several have continuing interest.

Polyimides are well known for their excellent thermal and oxidative stability, as well as exceptional mechanical properties. The need for thermally stable membranes has suggested the possibility of using polyimides with appropriate ion-conducting sites. However, normal five-membered ring phthalic polyimides display poor hydrolytic stability under the strongly acidic conditions of a fuel cell.[133] It is likely that acid catalyzed hydrolysis of the phthalimide structure leads to lowered molecular weight by

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[127] Miyatake, K.; Iyotani, H.; Yamamoto, K.; Tsuchida, E. Synthesis of Poly(phenylene sulfide sulfonic acid) via Poly(sulfonium cation) as a Thermostable Proton-Conducting Polymer. *Macromolecules*, **1996**, *29*, 6969-6971.

[128] Noshay, A.; Robeson, L.M. Sulfonated Polysulfone. *J. Appl. Polym. Sci.* **1976**, *20*, 1885-1903.

[129] Wang, F.; Hickner, M.; Kim, Y.S.; Zawodzinski, T.A.; McGrath, J.E. Direct Polymerizaton of Sulfonated Poly(arylene ether sulfone) Random (Statistical) Copolymers: Candidates for New Proton Exchange Membranes. *J. Membr. Sci.* **2002**, 197, 231-242.

[130] Asensio, J.A.; Borros, S.; Gomez-Romero, P. Proton-Conducting Polymers Based on Benzimidazoles and Sulfonated Benzimidazoles. *J. Polym. Sci.: Part A: Polym. Chem.* **2002**, 40, 3703-3710.

[131] Huang, R.Y.M.; Shao, P.; Burns, C.M.; Feng, X. Sulfonation of Poly(ether ether ketone) (PEEK): Kinetic Study and Characterization. *J. Appl. Polym. Sci.* **2001**, *82*, 2651-2660.

[132] Ghassemi, H.; McGrath, J.E. Proton-Conducting Polymers Derived From Poly(*p*-phenylene)s. *Div. Polym. Chem., Polym. Preprs.* **2002**, *43*, 1021-1022.

[133] Savadogo, O. Emerging Membranes for Electrochemical Systems: (I) Solid Polymer Electrolyte Membranes for Fuel Cell Systems. *J. New Mater. Electrochem. Systems* **1998**, *1*, 47-66.

chain scission and causes the membrane to become brittle.[134] Polyimides derived from bis(naphthalenic anhydrides), or six-membered ring polyimides, are less strained and have been reported to display better thermal and chemical stability, along with improved mechanical strength compared to the analogous five-membered ring counterparts.[135] Unfortunately, six-membered ring polyimides are more difficult to synthesize and cast into membranes due to their lower solubilities in common organic solvents.

Naphthalenic polyimides have been prepared by a high temperature polycondensation reaction in *m*-cresol. Six-membered ring anhydrides are more stable but their reactivity with an amine group is lower than that of their five-membered analogues. Therefore it is necessary to utilize catalysts in the reaction of such dianhydrides with diamines.[136] An acidic catalyst such as benzoic acid has been added in the first step, which is believed to promote formation of the *trans*-isoimide. It has been proposed that a basic catalyst is then needed to convert the *trans*-isoimide to a naphthalimide.[137]

Sulfonated six-membered ring polyimides have been synthesized by direct copolymerization, where a sulfonated diamine comonomer provides ion-conducting

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[134] Genies, C.; Mercier, R.; Sillion, B.; Petiaud, R.; Cornet, N.; Gebel, G.; Pineri, M. Stability Study of Sulfonated Phthalic and Naphthalenic Polyimide Structures in Aqueous Medium. *Polymer* **2001**, *42*, 5097-5105.

[135] Rusanov, A.L. Novel Bis(Naphthalic Anhydrides) and Their Polyheteroarylenes with Improved Processability. *Adv. Polym. Sci.* **1994**, *111*, 115-175.

[136] Sek, D.; Pijet, P.; Wanic, A. Investigation of Polyimides Containing Naphthalene Units: 1. Monomer Structure and Reaction Conditions. *Polymer* **1992**, *33*, 190-193.

[137] Sek, D.; Wanic, A.; Schab-Balcerzak, E. Investigation of Polyimides Containing Naphthalene Units. II. Model Compound Synthesis. *J. Polym. Sci.: Part A: Polym. Chem.* **1995**, *33*, 547-554.

sites.[138] The molar ratio of sulfonated to nonsulfonated diamine can be varied to produce copolymers with different degrees of sulfonation and hence ion exchange capacities (IEC). Previous researchers have mostly utilized 4,4'-diaminobiphenyl-2,2'-disulfonic acid (BDA), an available sulfonated diamine, to synthesize proton-conducting polyimides. Sulfonated polyimides based on BDA were reported to display limited stability in water.[139] Recently, several sulfonated naphthalenic polyimide copolymers have been synthesized from more flexible sulfonated diamines, which showed improved hydrolytic stability.[140,141] Commercially available 4,4'oxydianiline (ODA) and 9,9'-bis(4-aminophenyl)fluorene (BAPF) were sulfonated in fuming sulfuric acid to generate the desired sulfonated diamines, and these monomers were used to prepare high molecular weight film-forming sulfonated copolymers. Their improved stability in water was attributed to the higher basicity of the sulfonated diamine.

This paper reports the synthesis of a novel sulfonated diamine (3,3'-disulfonic acid-bis[4-(3-aminophenoxy)phenyl]sulfone, SA-DADPS) containing flexible sulfone and ether linkages to investigate the effects of structure and composition on hydrolytic

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[138] Cornet, N.; Diat, O.; Gebel, G.; Jousse, F.; Marsacq, D.; Mercier, R.; Pineri, M. Sulfonated Polyimide Membranes: A New Type of Ion-Conducting Membrane for Electrochemical Applications. *J. New Mater. Electrochem. Systems* **2000**, *3*, 33-42.

[139] Genies, C.; Mercier, R.; Sillion, B.; Cornet, N.; Gebel, G.; Pineri, M. Soluble Sulfonated Naphthalenic Polyimides as Materials for Proton Exchange Membranes. *Polymer* **2001**, *42*, 359-373.

[140] Fang, J.; Guo, X.; Harada, S.; Watari, T.; Tanaka, K.; Kita, H.; Okamoto, K. Novel Sulfonated Polyimides as Polyelectrolytes for Fuel Cell Application. 1. Synthesis, Proton Conductivity, and Water Stability of Polyimides from 4,4'-Diaminodiphenyl Ether-2,2'-disulfonic Acid. *Macromolecules* **2002**, *35*, 9022-9028.

[141] Guo, X.; Fang, J.; Watari, T.; Tanaka, K.; Kita, H.; Okamoto, K. Novel Sulfonated Polyimides as Polyelectrolytes for Fuel Cell Application. 2. Synthesis and Proton Conductivity of Polyimides from 9,9-Bis(4-aminophenyl)fluorene-2,7-disulfonic Acid. *Macromolecules* **2002**, *35*, 6707-6713.

stability and membrane ductility. Three series of sulfonated polyimide copolymers are discussed.

3.3. Experimental

3.3.1. Materials

4,4'-Dichlorodiphenyl sulfone (DCDPS) was kindly provided by Solvay Advanced Polymers. 1,4,5,8-Naphthalene tetracarboxylic dianhydride (NDA) was purchased from Aldrich and vacuum dried at 170 °C for 12 h before use. Bis[4-(3-aminophenoxy)phenyl] sulfone (*m*-BAPS) was purchased from TCI and recrystallized from ethanol. 4,4'-Oxydianiline (ODA), 1,3-phenylenediamine (*m*-PDA), and 3-aminophenol (*m*-AP) were purchased from Aldrich and sublimed under reduced pressure before use. *m*-Cresol (Aldrich) was distilled under reduced pressure over anhydrous P_2O_5 prior to use. Dimethylsulfoxide (DMSO) (Aldrich) was distilled under reduced pressure over calcium hydride. N-methyl-2-pyrrolidinone (NMP) (Fisher) was used without further purification. Triethylamine (TEA), benzoic acid (BA), isoquinoline (IQ), chlorobenzene, and fuming sulfuric acid (27% SO_3) were used as received from Aldrich.

3.3.2. Monomer Synthesis

3.3.2.1. Disodium-3,3'-disulfonate-4,4'-dichlorodiphenylsulfone (S-DCDPS)

The synthesis of S-DCDPS has been previously described.[142,143,144] In a typical reaction, DCDPS (28.7 g, 99 mmol) was dissolved in 60 mL (390 mmol SO_3) of fuming

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[142] Wang, F.; Hickner, M.; Ji, Q.; Harrison, W.; Mecham, J.; Zawodzinski, T.A.; McGrath, J.E. Synthesis of Highly Sulfonated Poly(arylene ether sulfone) Random (Statistical) Copolymers Via Direct Polymerization. *Macromol. Symp.* **2001**, *175*, 387-395.

sulfuric acid (27% SO_3) in a 100-mL, three neck flask equipped with a mechanical stirrer, condenser, and a nitrogen inlet/outlet. The solution was heated to 110 °C for 6 hours to produce a homogeneous solution. The reaction was cooled to room temperature, dissolved into 400 mL of ice water, and 180 g of sodium chloride were added to produce a white precipitate of the product. The powder was filtered, redissolved in 400 mL of deionized water and neutralized to a pH ~ 6-7 with aqueous 2 N sodium hydroxide. An excess of sodium chloride (~180 g) was added to salt out the sodium form of the disulfonated monomer. The crude S-DCDPS was filtered and purified by recrystallization from a mixture of isopropanol and water (6/1, v/v). The resulting pure product was dried at 120 °C under vacuum for at least 24 hours. Yield 36.8 g (75%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.33 ppm (d, 2H), 7.85 ppm (dd, 2H), 7.65 ppm (d, 2H); FT-IR (KBr) 1026 cm^{-1} (S=O, sulfonic acid, sym.), 1087 cm^{-1} (S=O sulfonic acid, asym.), 1168 cm^{-1} (S=O, sulfone); Mass Spectrum (FAB) 467 Daltons (S-DCDPS-Na$^+$); Elemental Analysis Calcd.: C, 27.3; H, 1.15; S, 18.2; Na, 8.72. Found: C, 27.4; H, 1.23; S, 19.3; Na, 9.36.

3.3.2.2. Disodium-3,3'-disulfonate-bis[4-(3-aminophenoxy)phenyl]sulfone (S-DADPS)

In a 500-mL, three neck flask equipped with a mechanical stirrer, Dean-Stark trap, condenser, and a nitrogen inlet/outlet, 21.83 g (0.2 mol) of 3-aminophenol, 8.0 g

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[143] Harrison, W.L.; Wang, F.; Mecham, J.B.; Bhanu, V.A.; Hill, M.; Kim, Y.S.; McGrath, J.E. Influence of the Bisphenol Structure on the Direct Synthesis of Sulfonated Poly(arylene ether sulfone) Copolymers. I. *J. Polym. Sci.: Part A: Polym. Chem.* **2003**, 41, 2264-2276.

[144] Ueda, M.; Toyota, H.; Ochi, T.; Sugiyama, J.; Yonetake, K.; Mazuko, T.; Teremoto, T. Synthesis and Characterization of Aromatic Poly(ether sulfone)s Containing Pendent Sodium Sulfonate Groups. *J. Polym. Sci.: Polym. Chem. Ed.* **1993**, *31*, 853-858.

(0.2 mol) of sodium hydroxide, 300 mL of distilled DMSO and 130 mL of chlorobenzene were added. The solution was allowed to reflux at 160 °C while the chlorobenzene azeotropically removed water. After 8 hours the chlorobenzene was removed and 47.42 g (0.09 mol) of S-DCDPS plus 20 mL of DMSO were added. The reaction temperature was increased to 170 °C for 24 hours, cooled to room temperature, and then filtered. The filtrate was precipitated in a large excess of isopropanol and the brown product was filtered and washed with isopropanol. The resulting product was dried at 120 °C under vacuum for at least 24 hours. Yield 62%; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.20 ppm (d, 2H), 7.79 ppm (dd, 2H), 6.95 ppm (t, 2H), 6.85 ppm (d, 2H), 6.37 ppm (dd, 2H), 6.15 ppm (m, 4H); FT-IR (KBr) 1036 cm^1 (S=O, sym.), 1078 cm^{-1} (S=O, asym.), 1151 cm^{-1} (S=O, sulfone), 1244 cm^{-1} (C-O-C); Mass Spectrum (FAB) 613 Daltons (S-DADPS-Na$^+$); Elemental Analysis Calcd.: C, 45.28; H, 2.85; N, 4.40; Na, 7.22; S, 15.11. Found: C, 42.22; H, 3.41; N, 4.10; Na, 7.20; S, 15.03.

3.3.2.3. 3,3'-Disulfonic acid-bis[4-(3-aminophenoxy)phenyl]sulfone (SA-DADPS)

HCl (37%, 8.29 g mole) was added drop-wise to a stirring solution of 26.75 g (0.042 mol) of S-DADPS in 270 mL of water. Upon complete addition, the mixture was stirred for a few minutes, filtered, and diluted with 2 L of isopropanol. The precipitate that formed was filtered and washed with isopropanol then acetone, and dried under vacuum at 120 °C for 24 hours. The crude SA-DADPS was recrystallized from deoxygenized water under nitrogen to produce monomer-grade material. Yield 92 %; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.30 ppm (d, 2H), 7.95 ppm (dd, 2H), 7.46 ppm (t, 2H), 7.03 ppm (d, 2H), 6.96 ppm (t, 4H), 6.75 ppm (t, 2H), 4.50 ppm (m, 4H); FT-IR (KBr)

1028 cm^1 (S=O, sulfonic acid, sym.), 1075 cm^{-1} (S=O sulfonic acid, asym.), 1140 cm^{-1} (S=O, sulfone), 1264 cm^{-1} (C-O-C); Mass Spectrum (FAB) 591 Daltons (SA-DADPS-H^+); Elemental Analysis Calculated.: C, 48.64; H, 3.40; N, 4.73; S, 16.23. Found: C, 47.07; H, 4.52; N, 4.51; S, 16.20.

3.3.3. Polymer Synthesis

3.3.3.1. Synthesis of *m*-BAPS/NDA homopolymer

NDA (4.0228 g, 15 mmol), *m*-BAPS (6.4875 g, 15 mmol) and benzoic acid (3.6636 g, 30 mmol) were added to a 250-mL, three neck flask equipped with a mechanical stirrer, Dean-Stark trap, condenser, and a nitrogen inlet/outlet. *m*-Cresol (95 g) was added to afford a concentration of 10% solids. The reaction mixture was heated at 80 °C for 4 h, and then at 180 °C for 9 h. Next, 3.8747 g (30 mmol) of isoquinoline were added to the reaction and it was heated at 180 °C for another 9 h. The reaction mixture was cooled to room temperature and precipitated into an excess of isopropanol. The precipitated polyimide was collected by filtration and purified in a Soxhlet extractor with methanol overnight. The resulting yellow, fibrous polymer (BAPS-00) was dried in a vacuum oven at 100 °C for 6 h and then at 150 °C for 24 h. Yield 98%; FT-IR (NMP cast film) 1716 cm^{-1} (C=O, sym.), 1678 cm^{-1} (C=O, asym.), 1349 cm^{-1} (C-N, sym.), 1253 cm^{-1} (S=O, sulfone).

3.3.3.2. Synthesis of disulfonated polyimide copolymers

A direct synthesis of a disulfonated polyimide copolymer with 60 mol % disulfonation (BAPS-60) is discussed. In a 250-mL, three neck flask equipped with a mechanical stirrer, Dean-Stark trap, condenser, and a nitrogen inlet/outlet, 5.3336 g (9.0 mmol) of SA-DADPS, 80 g of *m*-cresol and 2.1857 g (21.6 mmol) of triethylamine were added to form the soluble and more reactive derivative. The solution was stirred at room temperature for 4 hours until complete dissolution of the diamine. Then 4.0228 g (15.0 mmol) of NDA, 2.5950 g (6.0 mmol) of *m*-BAPS and 3.6636 g (30.0 mmol) of benzoic acid were added, along with 28 g of *m*-cresol to afford a concentration of 10% solids. The reaction mixture was heated at 80 ^{o}C for 4 h, and then at 180 ^{o}C for 9 h. Next, 3.8747 g (30.0 mmol) of isoquinoline were added to the reaction and it was heated at 180 ^{o}C for another 9 h. The reaction mixture was cooled to room temperature and precipitated into an excess of isopropanol. The precipitated polyimide copolymer was collected by filtration and purified in a Soxhlet extractor with methanol overnight. The resulting yellow, fibrous copolymer BAPS-60 was dried under vacuum at 100 ^{o}C for 6 h and then at 150 ^{o}C for 24 h. Yield 11.83 g (96 %); FT-IR (NMP cast film) 1716 cm^{-1} (C=O, sym.), 1678 cm^{-1} (C=O, asym.), 1349 cm^{-1} (C-N, sym.), 1029 cm^{1} (S=O, sym.), 1075 cm^{-1} (S=O, asym.), 1253 cm^{-1} (S=O, sulfone).

A practical nomenclature for the disulfonated polyimide copolymers described in this manuscript will be as follows. Three different nonsulfonated diamines were used to prepare copolymers with degrees of disulfonation ranging from 30% to 80%. The symbolism X-YY, where X refers to the nonsulfonated diamine and YY is the mole percent of SA-DADPS (degree of disulfonation), relative to the six-membered ring dianhydride, NDA, will be used. For example, ODA-40 describes the 4,4'-oxydianiline based disulfonated copolymer that incorporates 40 mol% of SA-DADPS and 60 mol% 4,4’-oxydianiline (ODA).

3.3.4. Membrane Preparation

A series of tough, ductile copolymer membranes was prepared with controlled thickness of 0.070 – 0.180 mm. The triethylammonium salt form of the copolymers were redissolved in NMP (5% w/v) at 25 – 40 ^{o}C, passed through a 0.45 μm PTFE membrane filter and directly cast onto clean glass substrates. They were first slowly dried with infrared heat at increasing temperatures under a nitrogen atmosphere. The membranes were removed from the glass substrates by submersing them in water and then vacuum-dried at 160 ^{o}C for at least 24 h. In all cases, transparent but reddish-brown membranes were obtained.

The copolymer membranes in their triethylammonium salt form were completely converted to the corresponding acid-form membranes with some difficulty by immersion in boiling 0.5 M H_2SO_4 for 2 hours and 1.5 M H_2SO_4 at room temperature for 3 days. An alternative acidification procedure involved immersing the triethylammonium salt form of the membranes in 1.5 M H_2SO_4 at room temperature for 10 days. All membranes were carefully washed with deionized water and dried.

3.3.5. Characterization

^{1}H and ^{13}C NMR spectra were recorded on a Varian Unity 400 instrument operating at 399.952 MHz and 100.578 MHz, repectively, in deuterated dimethylsulfoxide (DMSO-d_6). Infrared measurements were performed on a Nicolet

Impact 400 FT-IR Spectrometer from KBr pellets or solution cast films for monomers and polymer, respectively. Intrinsic viscosity (IV) measurements were conducted in NMP at 25 °C using a Cannon Ubbelohde viscometer. Gel permeation chromatography (GPC) was performed using LiBr/NMP at ambient temperature and a flow rate of 1.0 mL per minute. Weight-average and number-average molecular weights were calculated relative to polystyrene standards. Thermo-oxidative behavior of both the triethylammonium salt-form (sulfonate) and the acid-form of the copolymers was measured on a TA Instruments TGA Q 500. Samples were dried directly in the TGA furnace at 200 °C for 2 h prior to analysis to remove water. The copolymers were evaluated from 50 °C to 800 °C in air at a heating rate of 10 °C / minute. The ion-exchange capacities (IEC) of the acid forms of the membranes were determined by nonaqueous potentiometric titration using an MCI Automatic Titrator Model GT-05. The acidified membranes were dissolved in DMAc and titrated with a standard tetramethylammonium hydroxide (TMAH) solution.

3.4. Results and Discussion

3.4.1. Monomer Synthesis

Brode et al. previously demonstrated the preparation of a nonsulfonated sulfone-ether diamine (SED) by nucleophilic aromatic substitution.[145] The high purity SED was prepared by reacting 4,4'-dichlorodiphenylsulfone with the sodium salt of aminophenol in the presence of dimethylsulfoxide. Herein, a novel sulfonated diamine monomer, SA-

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[145] Kawakami, J.H.; Kwiatkow, G.T.; Brode, G.L.; Bedwin, A.W. High Temperature Polymers. I. Sulfone Ether Diamines as Intermediates for Tractable High Temperature Polymers. *J. Polym. Sci.: Part A: Polym. Chem.* **1974**, *12*, 565-573.

DADPS, was synthesized in a similar fashion by the reaction scheme shown in Figure 3-1. S-DCDPS was prepared by sulfonation of 4,4'-dichlorodiphenylsulfone using fuming sulfuric acid at 110 ^{o}C for 6 hours, as previously described. The electrophilic substitution reaction occurs *meta* to the sulfonyl group and *ortho* to the chlorine, due to electron withdrawing nature of the sulfone group. S-DADPS was prepared from the nucleophilic substitution reaction of S-DCDPS with *m*-aminophenol (*m*-AP), which was first treated with stoichiometric amounts of sodium hydroxide. The *m*-aminophenoxide was produced from the reaction of *m*-AP with base (NaOH) in DMSO at 160 ^{o}C. Water was generated as the by-product of the reaction and removed with chlorobenzene as an azeotroping agent. Once formation of the sodium salt of *m*-AP was complete, S-DCDPS was added and the temperature was raised to 170 ^{o}C to remove all of the azeotropic solvent, and to complete the formation of the diamine. ^{1}H NMR, FT-IR, elemental analysis, and mass spectrometry confirmed the molecular structure and composition of the sulfonated sodium salt compound, S-DADPS.

S-DADPS was converted to the acid form with stoichiometric amounts of dilute hydrochloric acid, and then precipitated into an excess of either acetone or isopropanol. The monomer grade product, SA-DADPS, was obtained by recrystallization from deoxygenized water under nitrogen. ^{1}H NMR, FT-IR, elemental analysis, and mass spectrometry confirmed the anticipated molecular structure and composition of the sulfonic acid form of the diamine. The ^{1}H NMR of SA-DADPS and structure assignments are shown in Figure 3-2.

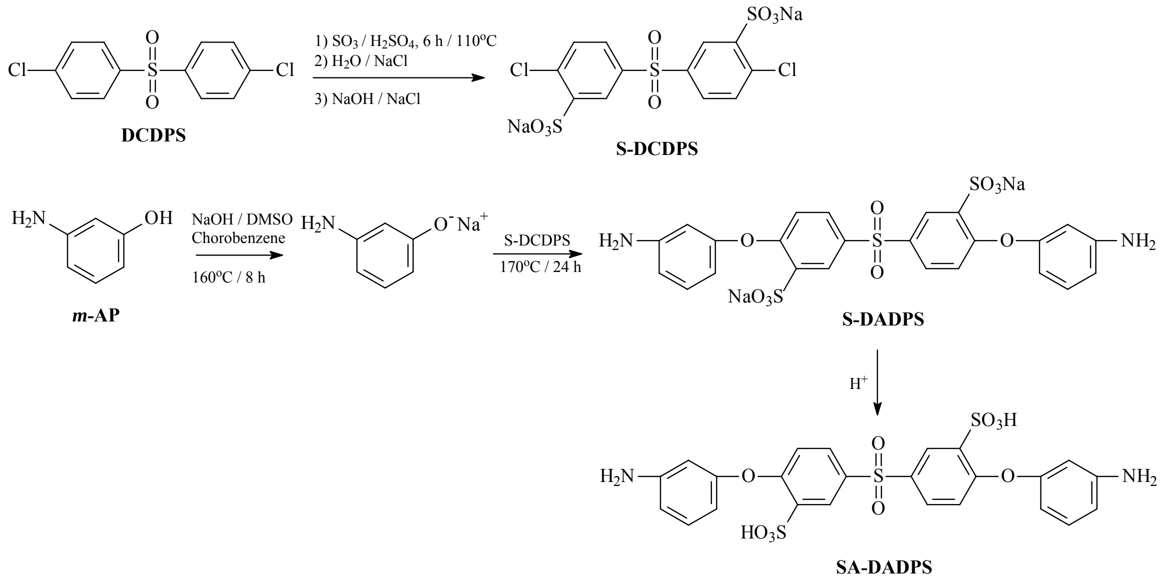

Figure 3-1. Synthesis of sulfonated diamine monomer (SA-DADPS)

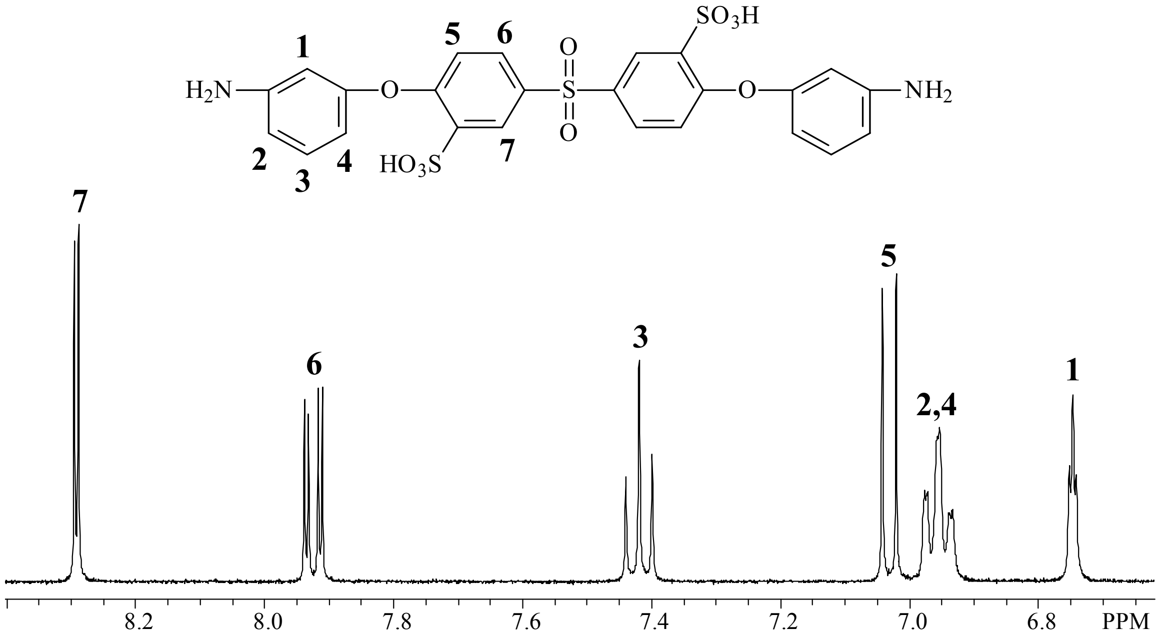

Figure 3-2. ^{1}H NMR spectrum and peak assignments of the SA-DADPS monomer (DMSO-d_6)

3.4.2. Copolymer Synthesis and Characterization

A one-pot, high temperature polycondensation method was used to synthesize six-membered ring copolyimides with controlled degrees of disulfonation (Figure 3-3). Although the high hydrolytic stability of the six-membered ring anhydride is desirable, its lower ring strain is also less reactive toward amines. The synthesis of six-membered ring polyimides has been reported to be successful at 180 – 190 °C in *m*-cresol, in the presence of catalysts.[146] High molecular weight polyimides were obtained when benzoic acid and isoquinoline were added sequentially as catalysts in the polymerization.

SA-DADPS was used to provide sulfonated sites along the copolymer backbone. By varying the molar ratio of sulfonated diamine to nonsulfonated diamine, copolymers from 30 to 80% disulfonation were obtained. Three series of sulfonated polyimide copolymers were prepared from SA-DADPS, 1,4,5,8-naphthalene tetracarboxylic dianhydride (NDA), and three nonsulfonated diamines: *m*-BAPS, ODA, and *m*-PDA. SA-DADPS was expected to be unreactive and had poor solubility in *m*-cresol; consequently the triethylammonium salt form of the sulfonated monomer was utilized in the copolymerizations. After reaction with the highly basic tertiary amine, triethylamine, at room temperature for several hours, the monomer was soluble in *m*-cresol. This not only allowed for copolymerization of SA-DADPS, but also produced the free, much more reactive non Zwitterion-like amine groups, which could then react with the dianhydride. Yellow, fibrous copolymers were obtained after reacting for 18 hours at 180 °C and upon precipitation into isopropanol. The residual catalyst and polymerization solvent were thoroughly removed by Soxhlet extraction in methanol. High molecular weight

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[146] Sek, D.; Wanic, A.; Schab-Balcerzak, E. J. Novel Approach to the Mechanism of the High-Temperature Formation of Naphthalimides. *Polymer* **1994**, *34*, 2440-2442.

disulfonated polyimide copolymers were obtained over the desired range of compositions. Relative molecular weights were determined by intrinsic viscosity (IV) and gel permeation chromatography (GPC) (Table 3-1).

For comparison, a high molecular weight homopolymer of *m*-BAPS and NDA (BAPS-00) was prepared by a similar procedure. Both monomers were charged to the reaction flask along with *m*-cresol and benzoic acid. After 9 hours at 180 ^{o}C, isoquinoline was added to the reaction and it was allowed to proceed for an additional 9 hours at 180 ^{o}C. The polymer was isolated in isopropanol and extracted with methanol to remove residual *m*-cresol and catalysts. Attempts to polymerize homopolymers based on ODA or PDA with NDA resulted in insoluble low molecular weight oligomers due to the premature precipitation.

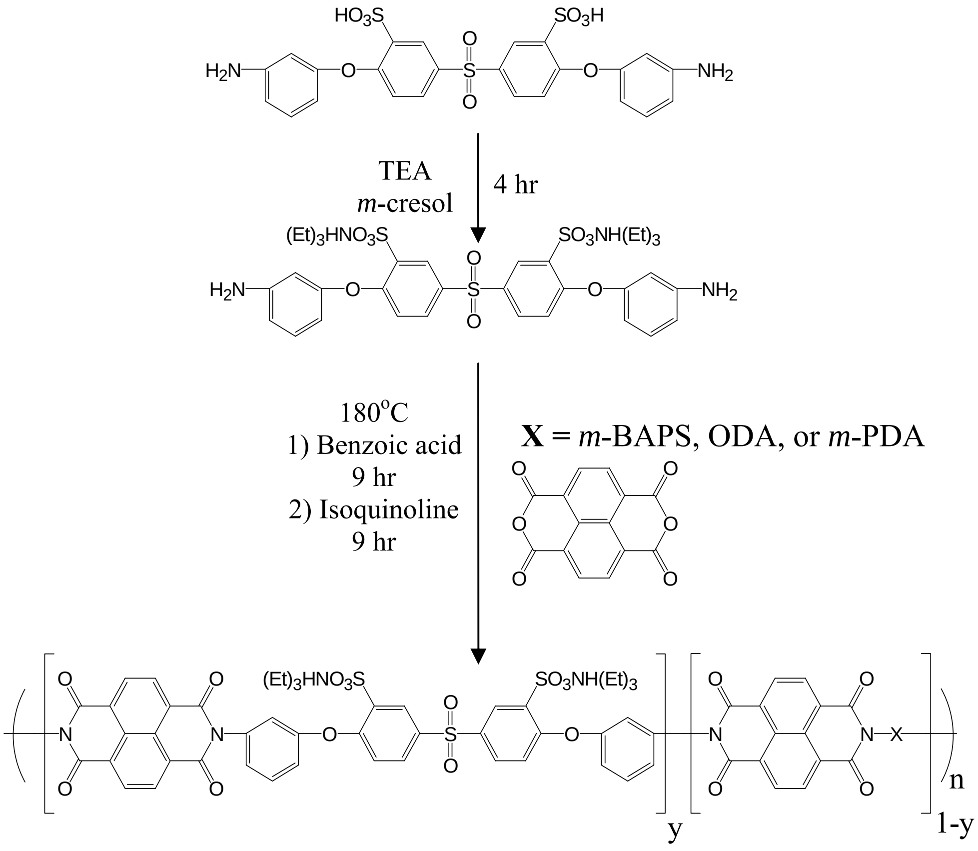


Figure 3-3. Synthesis of a disulfonated polyimide copolymer

Table 3-1. Properties of polyimides in their triethylammonium sulfonate salt form

Polymer	Yield	% Disulfonation by ^{1}H NMR	Intrinsic Viscosity* (dL g^{-1})	M_n** (g mol^{-1})	Polydispersity
BAPS-00	98	0	1.17	23,300	8.5
BAPS-30	95	32.6	2.17	34,200	6.1
BAPS-40	98	39.1	2.19	29,000	5.3
BAPS-50	97	49.3	2.40	28,400	4.5
BAPS-60	96	62.8	2.51	28,000	5.5
BAPS-70	97	75.6	1.54	27,000	3.6
BAPS-80	96	81.9	1.65	31,000	3.6
ODA-30	96	27.0	1.57	36,000	2.7
ODA-40	98	40.8	3.98	74,000	1.7
ODA-50	95	49.6	1.54	28,400	2.8
ODA-60	96	63.2	2.23	52,000	3.2
ODA-70	94	74.4	1.04	24,300	2.9
ODA-80	96	84.6	1.85	44,300	2.8
PDA-30	97	31.9	1.20	24,500	6.2
PDA-40	95	41.7	1.37	22,000	5.2
PDA-50	99	48.8	2.01	30,600	2.9
PDA-60	98	63.3	1.87	28,400	4.1
PDA-70	97	71.0	1.24	25,800	3.8
PDA-80	96	82.4	1.15	20,000	4.5

* NMP at 30 ^{o}C
** GPC compared to polystyrene standards

^1H NMR was used to identify the molecular structure of the sulfonated copolymers and evaluate the degree of disulfonation (Figure 3-4). The degree of disulfonation was determined from the ratio of a peak in the sulfonated region to one in both the sulfonated and nonsulfonated regions. Harrison et al. showed that the signal at 8.25 ppm represents the proton on the phenyl ring next to the sulfonated group. Genies et al. demonstrated that the set of peaks at 8.7 to 8.8 ppm correspond to the protons of the naphthalene ring and those in the triethylammonium sulfonate [$-SO_3NH(CH_2CH_3)_3$], respectively. The degree of disulfonation (mole % of disulfonated units) was determined by integrating these peaks and using the following formula:

$$\% \text{ Disulfonation} = 200\, H_c / (H_a + H_b - H_c)$$

As an example of the calculation, Figure 3-5 shows the integration of these peaks for ODA-50. The calculated degree of disulfonation from ^1H NMR is 48.2%, which is in good agreement with the amounts of monomers charged. The calculated values for the degree of disulfonation by ^1H NMR were determined for all copolymers (Table 3-1). The numbers match well with the feed ratios indicating that the incorporation of the sulfonated diamine was quantitative.

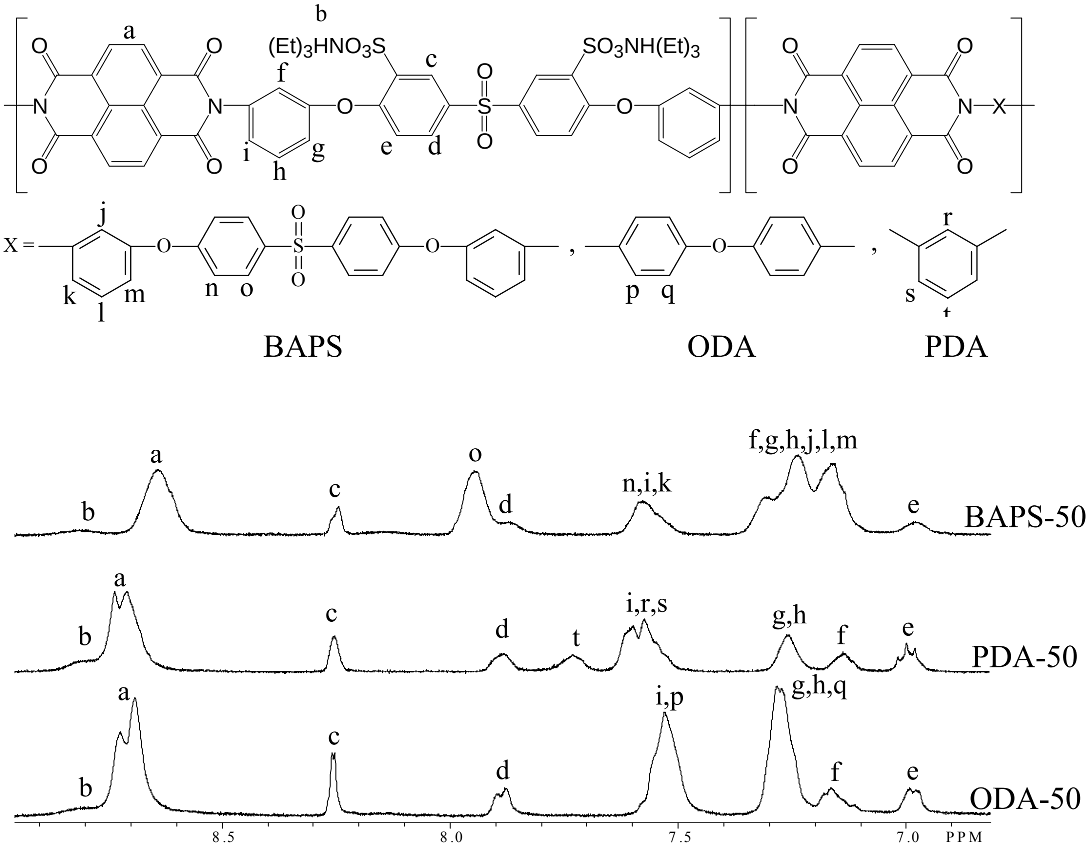
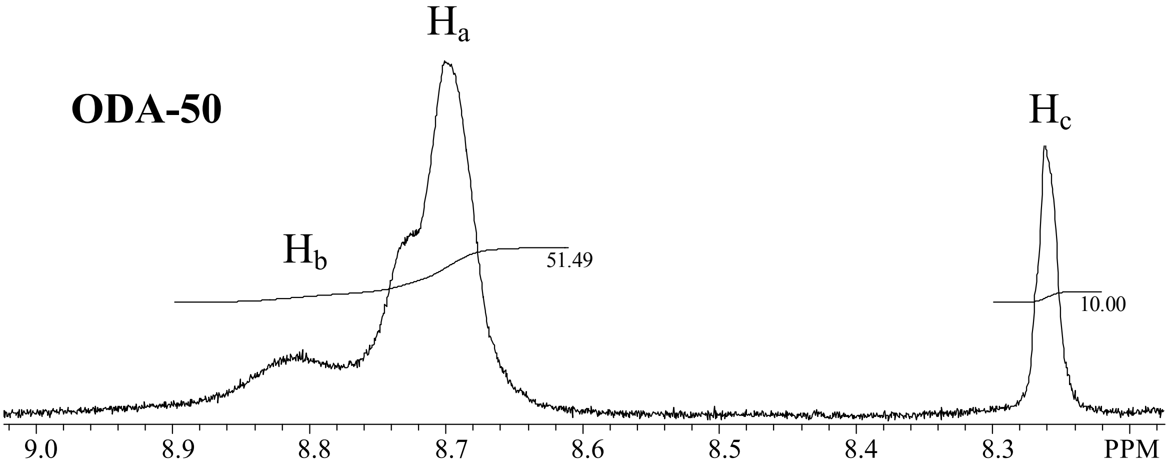


Figure 3-4. ^{1}H NMR spectra of polyimides in their triethylammonium sulfonate salt forms at 50% disulfonation (DMSO-d_6)



H_a and H_b represent 10 protons (6 sulfonated, 4 unsulfonated)
H_c represents 2 protons in the sulfonated domain

$$\begin{aligned}\textbf{\% Disulfonation} &= \mathbf{H_c / \{[(H_a + H_b - 3H_c) / 2] + H_c\}} \\ &= \mathbf{200\ H_c / (H_a + H_b - H_c)} \\ &= \mathbf{48.2\%}\end{aligned}$$

Figure 3-5. ^{1}H NMR and peak integrations of ODA-50

Tough, ductile membranes were prepared by dissolving the copolymers in their salt forms in NMP followed by casting onto clean, glass substrates. The solvent was evaporated under IR lamps in a nitrogen atmosphere. The membranes were separated from the glass plates by immersion in deionized water. Then the membranes were dried under vacuum to remove any residual solvent. Triethylammonium salt form membranes were converted to their corresponding acid forms using dilute sulfuric acid. Proper acidification conditions for sulfonated polyimides have not been previously discussed in the literature. Kim et al. explored two acidification methods, which were demonstrated to influence the conductivity and morphology of sulfonated poly(arylene ether sulfone) copolymer membranes.[147] The first method involved immersing the membranes in 1.5 M H_2SO_4 for 24 hours at room temperature, followed by washing in deionized water at room temperature for another 24 hours. The second method involved boiling the membranes in their salt forms in 0.5 M H_2SO_4 for 2 hours, then boiling them in deionized water for 2 hours. The sulfonated polyimide copolymers described herein were acidified by these two methods. ^{1}H NMR was used to determine the amount of repeat units with residual triethylammonium sulfonates in the membranes. Residual triethylammonium sulfonate peaks resonated at 1.1 ppm ($-CH_3$) and 3.1 ppm ($-CH_2$). After acidification, the residual triethylammonium sulfonate salt concentrations were surprisingly still 8.6 mol % (room temperature method) and 2.2 mol % (boiling method). Therefore it was necessary to establish new methods to quantitatively acidify the membranes to the sulfonic acid form, which is essential for proton conduction in a fuel cell. The

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[147] Kim, Y.S.; Wang, F.; Hickner, M.; McCartney, S.; Hong, Y.T.; Harrison, W.; Zawodzinski, T.A.; McGrath, J.E. Effect of Acidification Treatment and Morphological Stability of Sulfonated Poly(arylene ether sulfone) Copolymer Proton-Exchange Membranes for Fuel Cell Use above 100 ^{o}C. *J. Polym. Sci.: Part B: Polym. Phys.* **2003**, *41*, 2816-2828.

membranes in their triethylammonium sulfonate salt form were placed in boiling 0.5 M H_2SO_4 for 2 hours, then in 1.5 M H_2SO_4 at room temperature for 72 hours, and finally in room temperature deionized water for 24 hours. Using this method, the membranes were completely converted to their acid form, as shown by the disappearance of triethylammonium sulfonate salt peaks in the ^1H NMR. The membranes could also be converted to the sulfonic acid form by immersion in 1.5 M H_2SO_4 at room temperature for 10 days.

The solubilities of the copolymers in the acid form were studied in typical solvents such as NMP, DMAc, DMSO, methanol, acetone, and water (Table 3-2). All sulfonated copolymers demonstrated good solubility in polar aprotic solvents. However, the control homopolymer BAPS-00 was not soluble in DMSO. The sulfonated copolymers were generally insoluble in methanol, acetone and water, although a mixture of water and acetone (6:1, v/v) dissolved the highly sulfonated polyimides (BAPS-50 to BAPS-80).

Incorporation of the sulfonated diamine (degree of disulfonation) in the acidified copolymers was confirmed by ion-exchange capacity (IEC) measurements, FT-IR, and TGA. The calculated IECs[148] agreed with experimental values obtained from titration (Table 3-3).

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[148] Ion Exchange Capacity (IEC) = Degree of Disulfonation * 2 * 1000 / $Mass_{total}$
where $Mass_{total} = F_1$(MW of unsulfonated repeat unit) + F_2(MW of sulfonated repeat unit)
F_1 and F_2 are the respective molar ratio based on the charged diamines

Table 3-2. Solubilities of the BAPS series of disulfonated copolyimides in their triethylammonium salt form

Polymer	**Solvents**						
	NMP	DMSO	DMAc	MeOH	Acetone/Water (6:1 volume)	Acetone	Water
BAPS-00	+ +	− −	+ −	− −	− −	− −	− −
BAPS-30	+ +	+ +	+ +	− −	− −	− −	− −
BAPS-40	+ +	+ +	+ +	− −	− −	− −	− −
BAPS-50	+ +	+ +	+ +	− −	+ −	− −	− −
BAPS-60	+ +	+ +	+ +	− −	+ +	− −	− −
BAPS-70	+ +	+ +	+ +	+ −	+ +	− −	+ −
BAPS-80	+ +	+ +	+ +	+ −	+ +	− −	+ −

+ + : soluble at room temperature, + – : soluble by heating, – – : insoluble

Table 3-3. Properties of sulfonated polyimide copolymers in the sulfonic acid form

Polymer	Calculated IEC (meq g^{-1})	Experimental IEC by Titration (meq g^{-1})	Temperature at 5% Weight Loss (^{o}C)
BAPS-30	0.88	0.85	490
BAPS-40	1.12	1.02	484
BAPS-50	1.36	1.30	428
BAPS-60	1.59	1.50	422
BAPS-70	1.82	1.74	419
BAPS-80	2.03	1.90	390
ODA-30	1.09	1.05	450
ODA-40	1.36	1.25	436
ODA-50	1.58	1.56	426
ODA-60	1.80	1.72	140
ODA-70	1.98	1.94	400
ODA-80	2.14	2.01	395
PDA-30	1.24	1.20	438
PDA-40	1.50	1.53	384
PDA-50	1.72	1.60	381
PDA-60	1.90	1.94	370
PDA-70	2.06	2.05	365
PDA-80	2.20	2.17	360

Standardized FT-IR spectra allowed for determination of the functional groups in the copolymers. The spectra displayed the naphthalimide adsorption bands at 1716, 1678, and 1349 cm^{-1}, as well as those associated with the sulfonic acid groups. The symmetric and asymmetric stretches of the sulfonic acid groups appeared at 1030 and 1097 cm^{-1}, respectively. Figure 3-6 shows the FT-IR spectra for the BAPS series of polymers as a function of degree of disulfonation. The intensities of the peaks at 1030 and 1097 cm^{-1} increased with the degree of disulfonation. This trend was observed for all three sulfonated copolymer series.

The disulfonated copolymers were investigated by thermogravimetric analysis in both their salt and acidified forms. The membranes were analyzed between 30 and 800 ^{o}C at a heating rate of 10 ^{o}C / min in air (Figure 3-7). The acidified films displayed higher degradation temperatures than their corresponding triethylammonium sulfonate salt forms (Figure 3-8). A two-step degradation profile was observed for all sulfonated copolymers. The initial weight loss around 300 ^{o}C was assigned to desulfonation while the weight loss at 550 ^{o}C was attributed to the main chain polymer degradation. As the degree of disulfonation increased, the weight losses at about 300 ^{o}C increased and the degradation temperatures decreased. The nonsulfonated diamine comonomer structures had little to no effect on the thermo-oxidative stability.

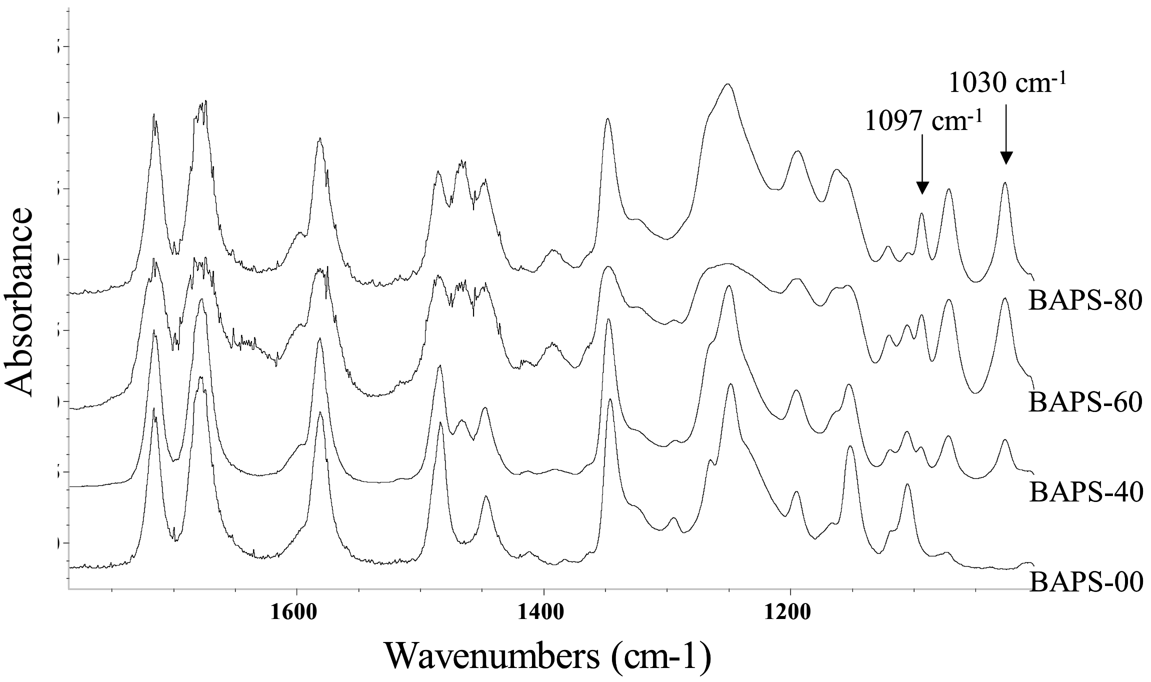

Figure 3-6. FT-IR spectra of the BAPS series of copolymers in their triethylammonium sulfonate salt form

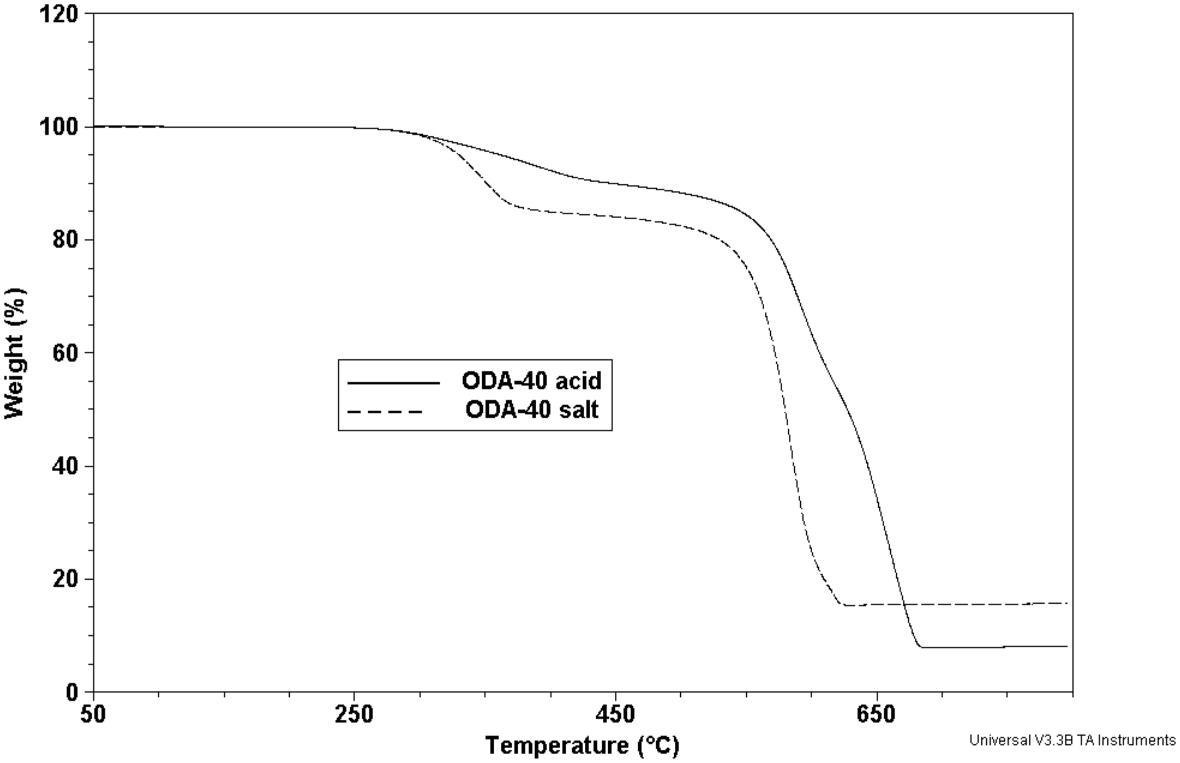

Figure 3-7. TGA profiles of triethylammonium sulfonate salt and sulfonic acid forms of ODA-40

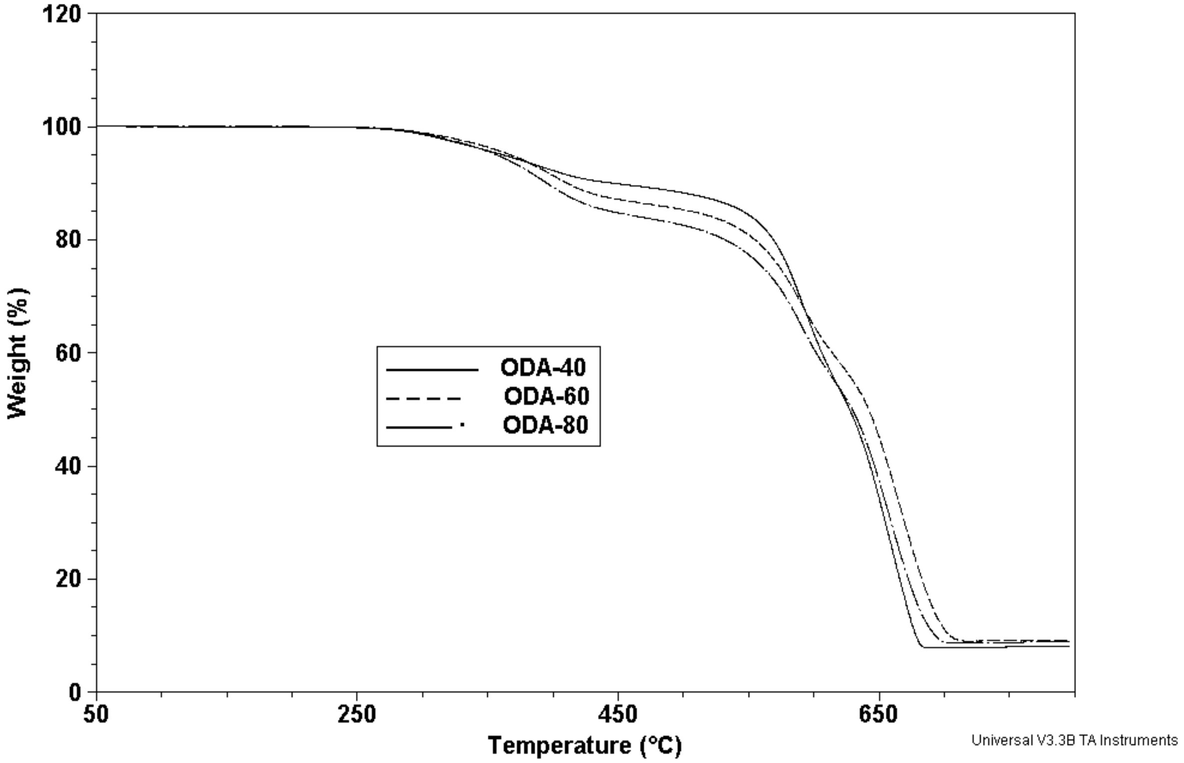

Figure 3-8. Influence of degree of disulfonation on the thermal stability of the ODA series of copolymers

3.5. Conclusions

A new method to prepare the novel disulfonated diamine, SA-DADPS, was developed. It was demonstrated that soluble, disulfonated six-membered ring copolyimides could be prepared from SA-DADPS, naphthalene tetracarboxylic dianhydride and three nonsulfonated diamines. Solution-cast films of these high performance polyelectrolytes were tough and ductile. Two methods for acidifying the membranes were established. The membranes were acidified by either soaking in boiling 0.5 M H_2SO_4 for 2 h, then in room temperature 1.5 M H_2SO_4 for 3 days, or in room temperature 1.5 M H_2SO_4 for 10 days. The structure-property relationships in these sulfonated polyimide copolymers will be the subject of a forthcoming paper.

3.6. Acknlowledgements

The authors would like to thank NASA Glenn (contract # NCC3-886) for their support of this research.

CHAPTER 4

SULFONATED NAPHTHALENE DIANHYDRIDE BASED POLYIMIDE COPOLYMERS FOR PROTON EXCHANGE MEMBRANE FUEL CELLS (PEMFC): II. MEMBRANE PROPERTIES AND FUEL CELL PERFORMANCE

Taken From:

Brian R. Einsla, Yu Seung Kim, Michael A. Hickner, Young-Taik Hong, Melinda L. Hill, Bryan Pivovar, James E. McGrath. Sulfonated Naphthalene Dianhydride Based Polyimide Copolymers for Proton Exchange Membrane Fuel Cells (PEMFC): II. Membrane Properties and Fuel Cell Performance. *Journal of Membrane Science* **2005**, *in press*.

4.1. Abstract

Selected properties of two series of sulfonated polyimide copolymers were studied to assess their potential for fuel cell applications. The copolyimides were synthesized in *m*-cresol from a novel disulfonated diamine, 3,3'-disulfonic acid-bis[4-(3-aminophenoxy)phenyl]sulfone (SA-DADPS), 1,4,5,8-naphthalenetetracarboxylic dianhydride (NDA), and one of two nonsulfonated diamines (4,4'-oxydianiline (ODA) or bis[4-(3-aminophenoxy)phenyl] sulfone (*m*-BAPS)) to produce tough, ductile films. The membrane parameters studied include water sorption, proton conductivity, water stability,

methanol permeability and direct methanol fuel cell (DMFC) performance. It was found that the choice of the nonsulfonated diamine significantly influenced the membrane stability in water at 80 °C. However, the water sorption and proton conductivity were a function of the ion exchange capacity and were independent of the structure of the nonsulfonated diamine. The copolyimide membranes utilizing *m*-BAPS as the nonsulfonated diamine displayed the best water stability at 80 °C. Unfortunately, the hydrolytic stability at 80 °C was still much lower than Nafion or analogous poly(arylene ether)s. At relatively high ion exchange capacities, the proton conductivities of the polyimides in water at 30 °C were equivalent to Nafion 1135. An IEC of ~1.9 (BAPS-80, ODA-70) was necessary to provide conductivities close to 0.1 S/cm in water at 30 °C. It was demonstrated that the proton conductivity of the membranes increased at elevated temperature and high relative humidity. The initial DMFC performance of several copolyimides was investigated, and it was found that these membranes had lower methanol permeability and performed comparably to Nafion 117.

4.2. Introduction

Recently, there has been considerable interest in the development of high performance and potentially lower cost proton exchange membrane (PEM) fuel cells for transportation, stationary and portable power applications.[149,150] The interest in fuel cells is largely due to their ability to continuously convert chemical energy into electric energy

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and heat with high efficiency and low emission of pollutants.[151] In PEM fuel cells, the membrane must transport protons from the anode to the cathode, and act as a barrier to oxygen and the hydrogen-rich fuel. At the anode, hydrogen is oxidized to protons and electrons by platinum or platinum/metal catalysts. The resulting protons are transported across the polymer electrolyte to the cathode. Useful electrical energy is harnessed by moving the electrons through an external circuit before allowing them to reach the cathode. At the cathode, gaseous oxygen from the air is reduced and combined with the protons and electrons to form water.[152]

Promising PEM fuel cell systems include high temperature hydrogen/air and direct methanol fuel cells (DMFC). In hydrogen/air-based fuel cells, high temperature (>120 ^{o}C) provides benefits such as faster electrode kinetics and greater tolerance to impurities in the fuel stream.[153] To operate at these high temperatures, new and improved mechanisms for conductivity above the boiling point of water are needed.[154] DMFCs offer reasonably high fuel energy density, readily stored liquid fuel, ease of refueling, and direct and complete electro-oxidation of methanol at moderate temperatures.[155] Perfluorosulfonic acid copolymers, such as Nafion®, are the state-of-the-art membranes for DMFC and hydrogen/air fuel cells due to their high conductivity when hydrated and

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superior chemical stability. However, there is much interest in alternative PEMs because of Nafion's reduced performance above 80 °C, significant methanol crossover and high cost.

One method to achieve proton conductivity in PEMs is to incorporate sulfonic acid sites along the polymer chain. As an example, sulfonated poly(arylene ether sulfone)s can be synthesized via post-sulfonation of the parent polymer, or direct copolymerization of sulfonated monomers. The properties of the resulting copolymer membrane depend on the preparation method as well as the processing steps.[156,157,158] Direct copolymerization of sulfonic acid-containing monomers allows for enhanced stability of the proton conducting sites, improved control of the ion-exchange capacity (IEC), and therefore control over the proton conductivity, water sorption, and morphology of the membrane.[159,160,161]

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Sulfonated six-membered ring (naphthalenic) polyimides are promising candidates for novel proton exchange membrane fuel cells. Due to their lower ring strain, six-membered ring polyimides have superior chemical and thermal stability compared to the more common five-membered ring polyimides.[162] Although five-membered ring polyimides have been investigated for use as PEMs,[163,164,165] the six-membered ring imide cycle was shown to be more hydrolytically stable.[166] It has been shown that sulfonated naphthalenic polyimides display promising hydrogen-air fuel cell performance and stability for more than 3000 hours at 60 °C.[167]

The synthesis of sulfonated six-membered ring polyimides for PEMs has been previously reported.[168,169] A direct copolymerization method was designed to synthesize polyimides with well-controlled degrees of disulfonation and block lengths. These copolymers offer the advantage of being prepared from commercially available

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monomers. More specifically, the rigid biphenyl sulfonated diamine, BDA, was used in the direct polymerization procedure as a source of ion-conducting sites along the polymer chain.

Disulfonated polyimides from novel sulfonated diamines have been prepared to examine the structure-property relationships of disulfonated six-membered ring copolyimides.[170,171] Specific diamines were chosen to improve the solubility and flexibility of the polyimide backbone. The water stability of the copolymers was improved by utilizing more flexible sulfonated and nonsulfonated diamines. Copolymers prepared from more basic sulfonated diamines also had enhanced water stability.[172,173] Additionally, random sulfonated copolyimides displayed better water stability than the block-type polymers, despite their lower conductivity.

The synthesis and characterization of sulfonated six-membered ring copolyimides based on the disulfonated diamine 3,3'-disulfonic acid-bis[4-(3-aminophenoxy)phenyl]sulfone (SA-DADPS) was reported.[174] SA-DADPS was prepared in an effort to improve the solubility and ductility of the resulting membranes. This

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chapter describes membrane properties important to fuel cell performance of two series of polyimide copolymers prepared from SA-DADPS, 1,4,5,8-naphthalenetetracarboxylic dianhydride (NDA), and two nonsulfonated diamines (Figure 4-1). The water sorption, conductivity, water stability, methanol permeability and initial fuel cell performance of the membranes are discussed.

4.3. Experimental

4.3.1. Sample Preparation

Sulfonated copolyimides were prepared by direct copolymerization of sulfonated and nonsulfonated monomers in *m*-cresol. The detailed synthetic procedures and characterization of these copolymers has been reported.,[175] Membranes were prepared by dissolving the copolymers in NMP (5% w/v) at 25 – 40 °C. The solutions were passed through a 0.45 μm PTFE membrane filter and directly cast onto clean glass substrates. They were first slowly dried under infrared heat at increasing temperatures under a nitrogen atmosphere. The membranes were removed from the glass plates by submersing them in water and then were vacuum-dried at 160 °C for at least 24 h. In all cases, transparent reddish-brown membranes were obtained. The copolymer membranes in their triethylammonium sulfonate salt form were completely converted to the corresponding sulfonic acid-form membranes by immersion in boiling 0.5 M H_2SO_4 for 2 h and 1.5 M H_2SO_4 at room temperature for 3 days. The conversion was confirmed by ^1H NMR. All membranes were carefully washed with deionized water and dried.

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[175] Hong, Y.T.; Einsla, B.; Kim, Y.S.; McGrath, J.E. Synthesis and Characterization of Sulfonated Polyimides Based on Six-Membered Ring as Proton Exchange Membranes. *ACS Div. Polym. Chem., Polym. Preprs.* **2002**, *43*, 666-667.

4.3.2. Membrane Electrode Assembly Fabrication

Membrane electrode assemblies (MEAs) for all membranes were prepared with standard Nafion-based electrodes using a direct painting method developed at Los Alamos National Laboratory.[176] Catalyst loadings were approximately 6 mg/cm^2 of unsupported platinum on the cathode, and 10 mg/cm^2 of unsupported platinum/ruthenium on the anode. To prepare the catalyst ink mixtures, a 5% Nafion dispersion (1100 equivalent weight) was added to the water-wetted catalysts. The anode ink composition was 86 wt % 1:1 platinum/ruthenium (JohnsonMatthey) and 14 wt % Nafion. The cathode ink composition was 90 wt % platinum (JohnsonMatthey) and 10 wt % Nafion. Catalyst inks were mixed by sonication for 1 min. and then directly painted on to a pre-dried membrane at 75 ^{o}C.

4.3.3. Characterization

Intrinsic Viscosity (IV) measurements were conducted in NMP at 30 ^{o}C with a Cannon-Ubbelohde viscometer. The water sorption values of the sulfonated polyimide copolymers were determined at 30 ^{o}C. The membranes were vacuum-dried at 120 ^{o}C for 24 h, weighed and immersed in deionized water at room temperature for 24 h. The wet membranes were wiped dry and quickly weighed again. The water uptake of the membranes was calculated in weight percent as follows:

$$water\ uptake = [(mass_{wet} - mass_{dry}) / mass_{dry}] * 100$$

Proton conductivity measurements were performed on membranes after being soaked in deionized water for 3 days at 30 ^{o}C. An impedance spectrum was recorded from 10 MHz

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[176] Thomas, S.C.; Ren, X.; Gottesfeld, S.; Zelenay, P. Direct Methanol Fuel Cells: Progress in Cell Performance and Cathode Research. *Electrochim. Acta* **2002**, *47*, 3741-3748.

to 10 Hz using a Hewlett-Packard 4129A Impedance/Gain-Phase Analyzer. The cell geometry was chosen to ensure that the membrane resistance dominated the response of the system. The resistance of the membrane was taken at the frequency which produced the minimum imaginary response. All impedance measurements were performed under fully hydrated conditions. The proton conductivity was taken as the reciprocal of the resistance and reported in units of Siemens per centimeter (S/cm). High temperature (70 – 140 ^{o}C) conductivity measurements were conducted in a modified pressure vessel. For measuring conductivity at elevated temperature, the cell was placed above liquid water in the pressure vessel, which afforded a saturated water-vapor environment. Once the membrane equilibrated with saturated water vapor at the desired temperature, the proton conductivity was measured using the Hewlett Packard Impedance Analyzer. The proton conductivities of polyimide membranes were also measured as a function of relative humidity (35 – 100%) at 80 ^{o}C. Samples were placed in the conductivity cell in an ESPEC SH-240 temperature and humidity controlled oven. When the humidity level in the oven was changed, the membranes were equilibrated for 8 h before any conductivity measurements were taken. This procedure ensured that the moisture levels inside the membranes were in equilibrium with the environment. The methanol permeability of each acid form membrane was determined in a standard membrane separated diffusion cell. This method has been reported previously[177,178] and the numerical analysis of this

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[177] Hickner, M.; Wang, F.; Kim, Y.S.; Zawodzinski, T.A.; McGrath, J.E. In *Proceeding of the AIChE Topical Conference*, Spring National Meeting, New Orleans, LA, March 10-14, 2002.

[178] Kim, Y.S.; Hickner, M.A.; Dong, L.; Pivovar, B.S.; McGrath, J.E. Sulfonated Poly(arylene ether sulfone) Copolymer Proton Exchange Membranes: Composition and Morphology Effects on the Methanol Permeability. *J. Membr. Sci.* **2004**, *243*, 317-326.

experiment has been outlined by Cussler.[179] Direct methanol fuel cell (DMFC) performance of the MEAs was tested using standard serpentine channel 5cm^2 Fuel Cell Technologies (Albuquerque, NM) fuel cell hardware with E-Tek (De Nora North America, Inc., Somerset, NJ) ELAT® gas diffusion backings. Methanol (diluted with Millipore 18.5 MΩ water) was supplied to the anode compartment at 1.8 mL/min. Air humidified to 10 °C above cell temperature was introduced to the cathode at a flowrate of 500 cm^3/min. The anode and cathode cell outlets were maintained at ambient pressure. All tests were conducted at Los Alamos National Laboratory at an elevation of 7,500 feet above sea level.

4.4. Results and Discussion

4.4.1. Membrane Preparation and Acidification

The preparation of the polyimide copolymers from SA-DADPS, NDA, and either 4,4'-oxydianiline (ODA) or bis[4-(3-aminophenoxy)phenyl] sulfone (*m*-BAPS) as the nonsulfonated diamines was previously reported (Figure 4-1). The molar ratio of sulfonated to nonsulfonated diamine was varied to prepare copolymers with degrees of disulfonation ranging from 30 to 80%. This yielded copolymers with ion-exchange capacities (IECs) ranging from 0.88 to 2.01 meq/g, corresponding to equivalent weights from 1140 to 470, respectively. The sulfonated copolymers were polymerized in their triethylammonium salt form to improve the solubility and reactivity of the sulfonated diamine. Tough, creasible, transparent membranes were obtained by solution casting and

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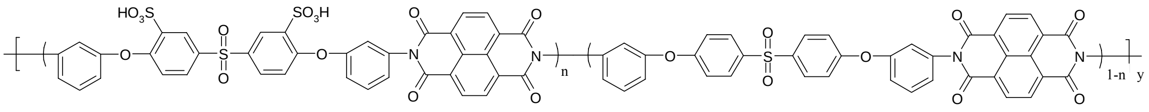
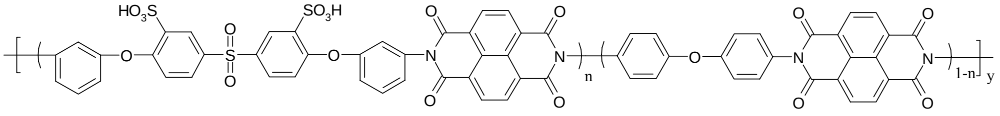
[179] Cussler, E.L. *Diffusion Mass Transfer in Fluid Systems*, 2nd Ed.; Cambridge University Press: New York, 1997.

completely converted to their sulfonic acid form by boiling 0.5 M H_2SO_4 for 2 h, then in room temperature 1.5 M H_2SO_4 for three days.



BAPS-XX



ODA-XX

Figure 4-1. Structures of sulfonated polyimide copolymers using SA-DADPS as the sulfonated diamine (XX = 100·n)

4.4.2. Water Sorption

The water sorption of sulfonated polymers is known to have a profound effect on membrane conductivity and mechanical properties.[180] Membranes with little water uptake typically have low proton conductivity, while the mechanical strength is compromised in membranes with high water sorption.[181] This mechanical instability is the result of a morphological change at the percolation threshold in which the hydrophilic domains become interconnected. The water content in ionomers is typically represented by both the water uptake and the number of water molecules per SO_3^- (λ). The equilibrium water sorption of these polyimides increased with increasing ion exchange capacity (IEC) due to the strong hydrophilicity of the sulfonic acid groups (Table 4-1). At a given IEC, both series of sulfonated copolyimides displayed comparable water uptakes. In previous work, sulfonated six-membered ring polyimides showed no change in the number of water molecules per sulfonic acid group (λ) with varying IEC. Polyimide copolymer membranes were cast directly from the polymerization solvent, and then methanol was used to remove the remaining catalysts and solvent. Finally, the membranes were acidified at room temperature in 0.1 M HCl. Unlike these previously studied polyimides, in this research λ increased with IEC for the copolymer membranes. Perhaps this effect may be due to differences in molecular structure, membrane preparation and acidification procedures. Nevertheless, the increase in λ with IEC is consistent with expectations and with experience with wholly aromatic sulfonated

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[180] Kopitzke, R.W.; Linkous, C.A.: Anderson, H.R.; Nelson, G.L. Conductivity and Water Uptake of Aromatic-Based Proton Exchange Membrane Electrolytes. *J. Electrochem. Soc.* **2000**, 147, 1677-1681.

[181] Gao, Y.; Robertson, G.P.; Guiver, M.D.; Jian, X. Synthesis and Characterization of Sulfonated Poly(phthalazinone ether ketone) for Proton Exchange Membrane Materials. *J. Polym. Sci.: Part A: Polym. Chem.* **2003**, *41*, 497-507.

poly(arylene ether sulfone)s that were isolated and cast in a similar procedure to the copolymers described herein.[182]

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[182] Kim, Y.S.; Dong, L.; Hickner, M.A.; Glass, T.E.; Webb, V.; McGrath, J.E. State of Water in Disulfonated Poly(arylene ether sulfone) Copolymers and a Perfluorosulfonic Acid Copolymer (Nafion) and Its Effect on Physical and Electrochemical Properties. *Macromolecules* **2003**, *36*, 6281-6285.

Table 4-1. Ion-exchange capacity, water uptake, and proton conductivity data for the disulfonated polyimide copolymers

Copolymer	IEC (meq g^{-1})	Equivalent Weight (g meq^{-1})	Water Uptake (%)	λ (H_2O molecules/SO_3^-)	Conductivity* (S cm^{-1})
BAPS-30	0.88	1140	19	12	0.01
BAPS-40	1.12	890	29	14	0.03
BAPS-50	1.36	730	38	15	0.04
BAPS-60	1.59	630	53	18	0.05
BAPS-70	1.82	550	65	20	0.09
BAPS-80	2.03	490	91	25	0.12
ODA-30	1.09	920	22	11	0.03
ODA-40	1.36	730	32	13	0.04
ODA-50	1.58	630	43	15	0.05
ODA-60	1.80	550	57	18	0.07
ODA-70	1.98	500	71	20	0.11
ODA-80	2.14	470	102	26	0.12
Nafion 1135	0.91	1100	19	22	0.11

*** Measurements were conducted in water at 30 °C**

4.4.3. Proton Conductivity

In PEM fuel cells the proton conductivity of the membrane is particularly important since it has a significant role in the performance of the fuel cell. Higher levels of proton conductivity allow higher power densities to be achieved. The proton conductivities for the sulfonated polyimide copolymers were determined using the cell geometry shown in Figure 4-2. In copolymer membranes with pendent sulfonic acid groups, the membrane must be hydrated for efficient proton conduction to occur. Therefore, the conductivity measurements of the membranes in their acid form were performed in liquid water at 30 ^{o}C. Both copolymer systems showed similar conductivity values at comparable IECs (Table 4-1). The proton conductivity of the copolymers increased with the degree of disulfonation, or IEC, due to the higher concentration of sulfonic acid groups.[183] Nafion 1135 (IEC ~0.91) was measured under the same conditions and resulted in a value of 0.11 S/cm, which agrees well with previous results.[184] At high levels of sulfonation, the conductivities of the polyimides were near or above that of Nafion 1135. An IEC of ~1.9 (BAPS-80, ODA-70) was necessary to provide conductivities close to 0.1 S/cm. The polyimide copolymers may require higher IECs to achieve the same conductivity as Nafion 1135 due the lower acidity of the aromatic sulfonic acid groups attached to the polyimide chain.

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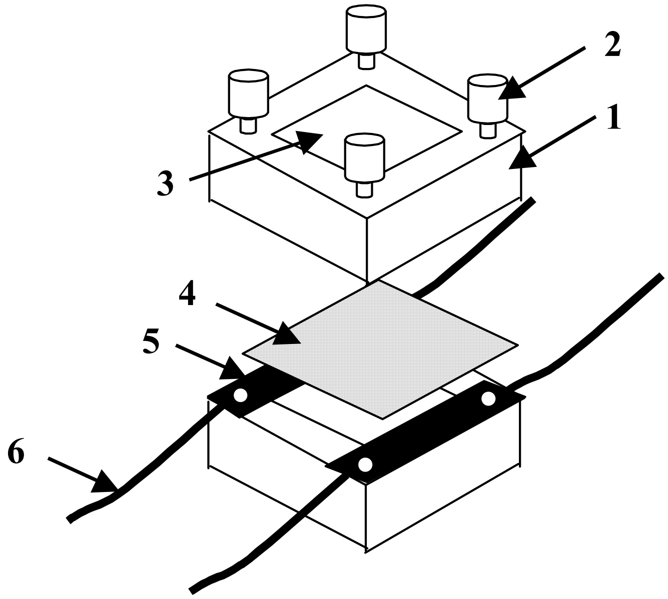
[183] Nolte, R.; Ledjeff, K.; Bauer, M.; Mulhaupt, R. Partially Sulfonated Poly(arylene ether sulfone) – A Versatile Proton Conducting Membrane Material for Modern Energy Conversion Technologies. *J. Membr. Sci.* **1993**, *83*, 211-220.

[184] Slade, S.; Campbell, S.A.; Ralph, T.R.; Walsh, F.C. Ionic Conductivity of an Extruded Nafion 110 EW Series of Membranes. *J. Electrochem. Soc.* **2002**, *142*, A1556-A1564.



Legend

1. Teflon block
2. Thumbscrew
3. Open area to allow equilibration with environment
4. Membrane sample
5. Blackened Pt foil electrode
6. Pt lead

Figure 4-2. Cell geometry of proton conductivity cell with labeled components

High temperature proton conductivity data is given for two sulfonated polyimide copolymers, BAPS-60 and ODA-40 (Figure 4-3). The membranes were tested from 70 to 140 ^{o}C at 100 % relative humidity in a modified pressure vessel (Figure 4-4). The conductivity of the membranes increased with temperature, which was consistent with other sulfonated polyimide systems.[185] Temperature had a larger effect on the conductivity of the polyimide membranes than Nafion 1135, consistent with observations of Alberti, et al. with sulfonated PEEK. BAPS-60 displayed the same conductivity as Nafion 1135 at 110 ^{o}C, though it dropped off when the temperature increased. This decline in conductivity may correspond to the hydrated T_g of BAPS-60.[186] ODA-40 showed the lowest conductivities of the membranes tested at high temperature possibly due to its reduced IEC. Yet at 140 ^{o}C and 100% relative humidity, ODA-40 provided the same conductivity as Nafion 1135, and showed no indication of conductivity decline over this temperature range.

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[185] Miyatake, K.; Zhou, H.; Uchida, H.; Watanabe, M. Highly Proton Conductive Polyimide Electrolytes Containing Fluorenyl Groups. *Chem. Commun.* **2003**, *3*, 368-369.

[186] Kim, Y.S.; Wang, F.; Hickner, M.; McCartney, S.; Hong, Y.T.; Harrison, W.; Zawodzinski, T.A.; McGrath, J.E. Effect of Acidification Treatment and Morphological Stability of Sulfonated Poly(arylene ether sulfone) Copolymer Proton-Exchange Membranes for Fuel Cell Use above 100 ^{o}C. *J. Polym. Sci.: Part B: Polym. Phys.* **2003**, *41*, 2816-2828.

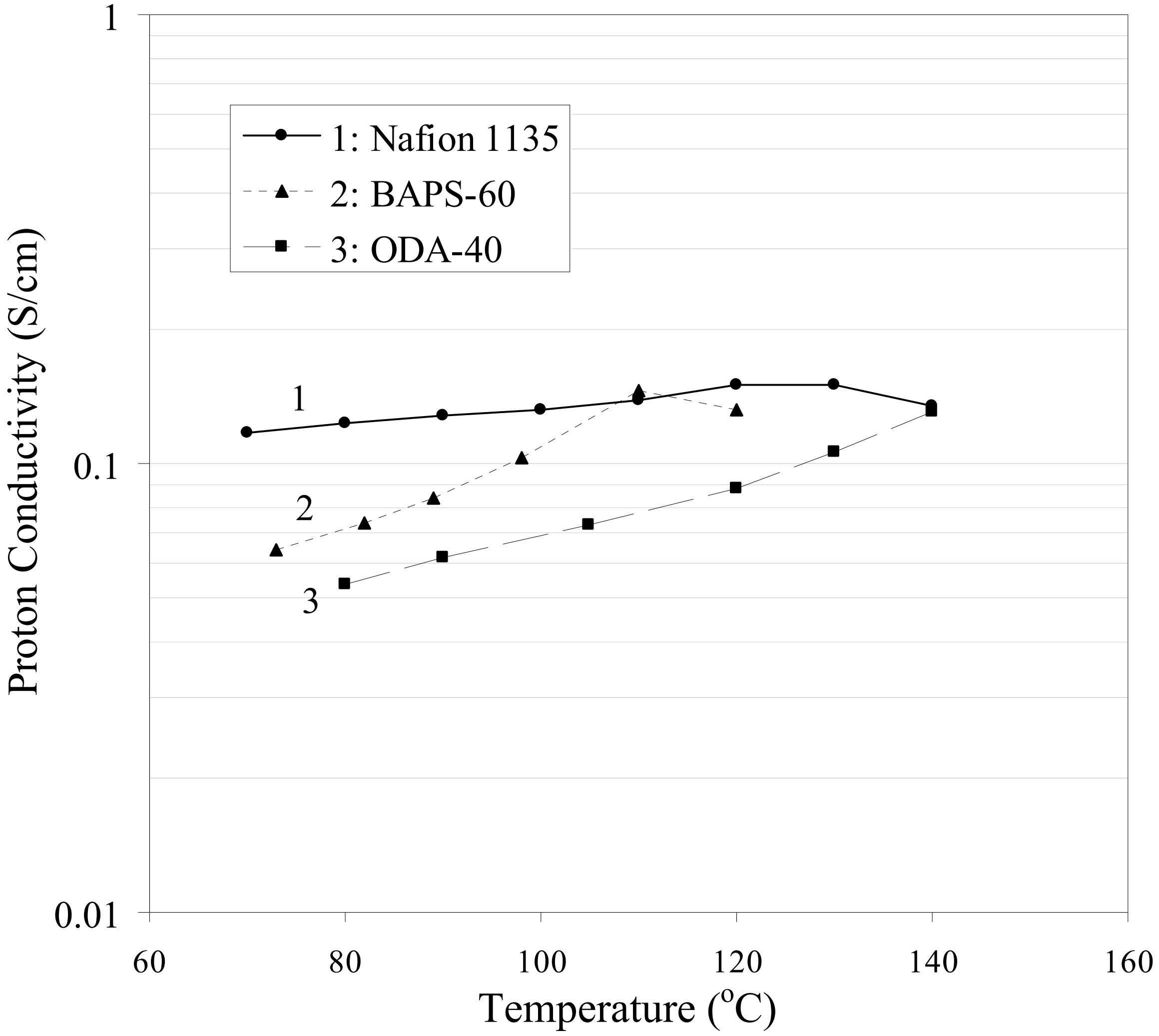

Figure 4-3. Proton conductivity of BAPS-60, ODA-40 and Nafion 1135 at elevated temperature

Previous results have shown that the relative humidity of a membrane has a significant effect on the proton conductivity.,[187,188] The proton conductivities of BAPS-50, ODA-60, and Nafion 1135 were tested at different humidity levels using a humidity/temperature oven at 80 ^{o}C (Figure 4-5). The conductivities of all three membranes increased with relative humidity, though the change in humidity had much more of an impact on the polyimides than Nafion 1135. Miyatake et al. showed a similar trend with sulfonated polyimides containing 1,5-naphthalene moieties.[189] It is interesting to note that at 80 ^{o}C and 90% relative humidity, the proton conductivities of the two sulfonated copolyimides were comparable to Nafion 1135, even though BAPS-50 and ODA-60 had lower conductivities at room temperature, 0.041 and 0.074 S/cm, respectively.

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[187] Sumner, J.J.; Creager, S.D.; J.J.; Ma, A.; DesMarteau, D.D. Proton Conductivity in Nafion 117 and in a Novel Bis[(perfluoroalkyl)sulfonyl]imide Ionomer Membrane. *J. Electrochem. Soc.* **1998**, *145*, 107-110.

[188] Sone, Y.; Ekdunge, P.; Simonsson, D. Proton Conductivity of Nafion 117 as Measured by a Four-Electrode AC Method. *J. Electrochem. Soc.* **1996**, *143*, 1254-1259.

[189] Miyatake, K.; Asano, N.; Watanabe, M. Synthesis and Properties of Novel Sulfonated Polyimides Containing 1,5-Naphthylene Moieties. *J. Polym. Sci.: Part A: Polym. Chem.* **2003**, *41*, 3901-3907.

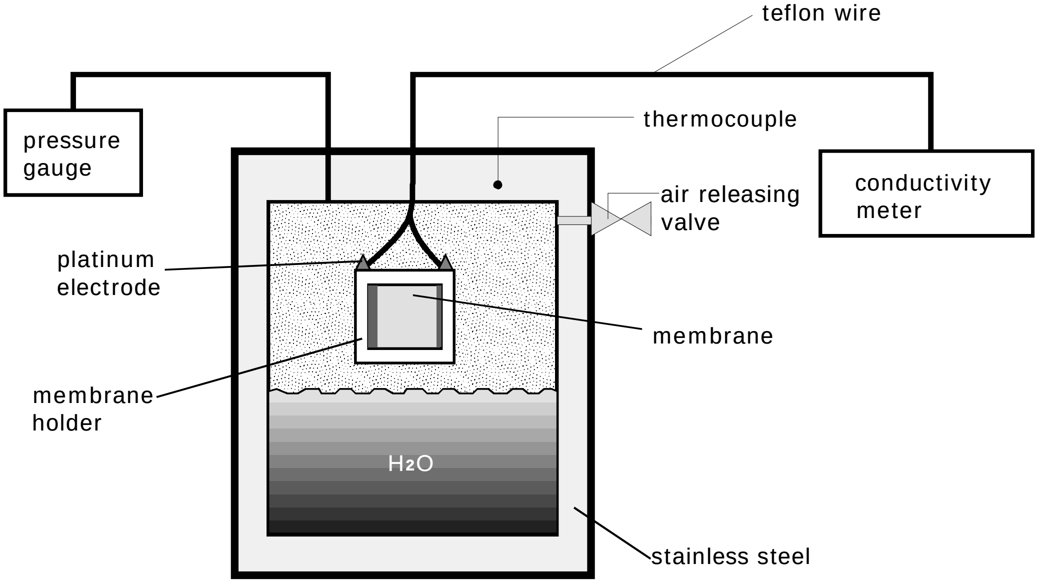

Figure 4-4. Pressure vessel for high temperature conductivity measurements

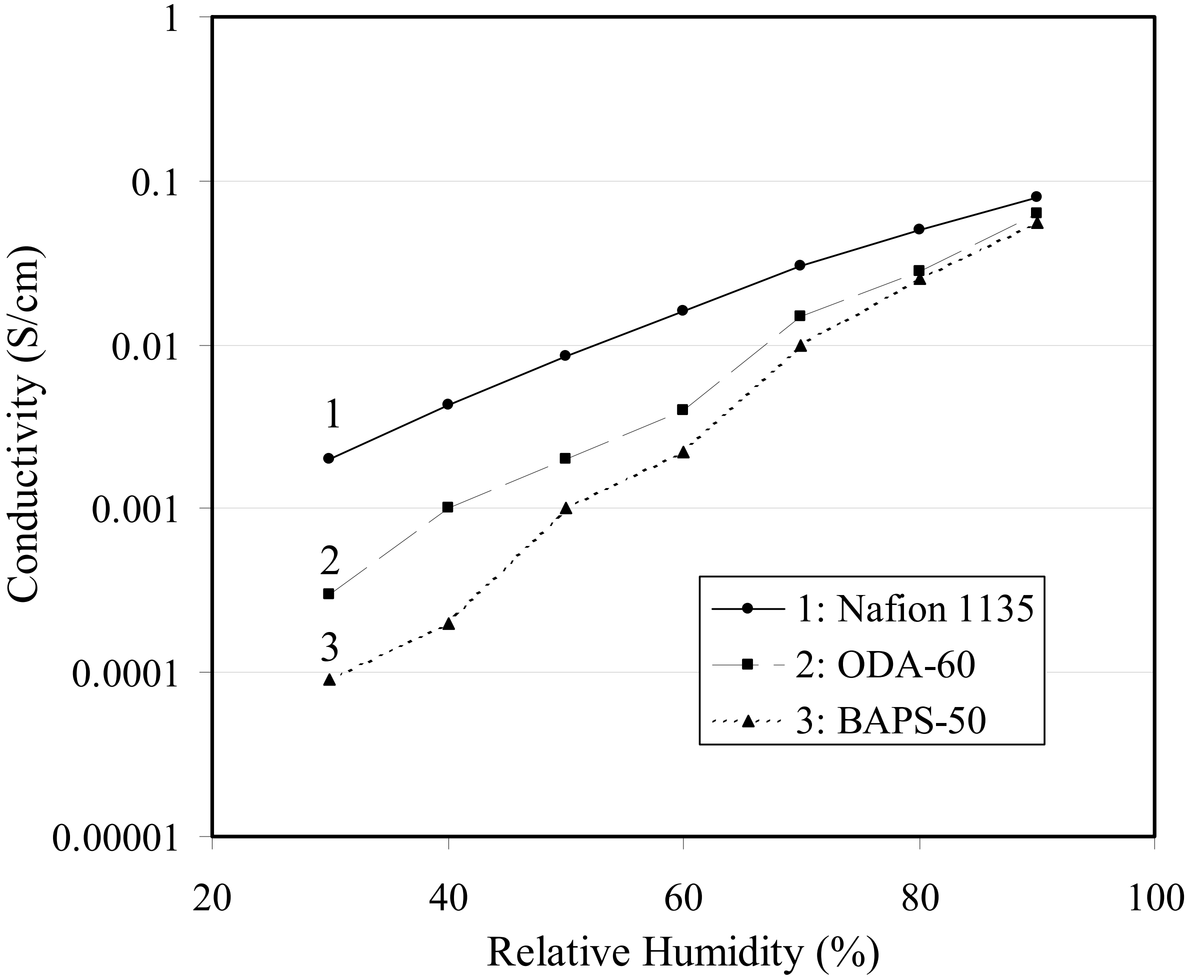

Figure 4-5. Effect of relative humidity on proton conductivity for BAPS-50, ODA-60 and Nafion 1135 at 80 ^{o}C

4.4.4. Water Stability

The stability of sulfonated polyimide membranes in water is intrinsically suspect and has been the subject of much research.[169-172] Although the improved stability of six-membered ring polyimides over the more common five-membered ring polyimides has been largely discussed,[166,167] the influence of structure on membrane stability has not. The water stability of these sulfonated polyimide copolymer membranes was tested by methods previously discussed and outlined in the experimental section.[171] The acid-form membranes were placed in deionized water at 80 °C until they became brittle. The loss of mechanical strength was determined when the membrane broke after being lightly bent. Additionally, in this paper, the "intrinsic viscosity" (IV) in pure NMP of the copolymers was recorded before and after the hydrolytic stability test. All of the polyimide copolymers displayed a significant decrease in IV after the membranes became brittle (Table 4-2). Since the IV is related to the chemical composition and molecular weight of the copolymer, one may conclude that the membranes became brittle due to hydrolytically induced random chain scission.

Within a series of copolymers, membranes with higher IECs became brittle faster (Table 4-2). The nature of the nonsulfonated diamine had a significant impact on the stability of the copolymer membrane in water. The nonsulfonated diamines (BAPS and ODA) were chosen to determine the effect of the diamine structure on water stability. The enhanced flexiblility in *m*-BAPS was achieved by incorporating ether and sulfone linkages coupled with the *meta* links between the oxygen atoms and amine groups. Although ODA is a desirable monomer due to its availability and economical cost, it is the more rigid of the two. Accordingly, the ODA copolymers displayed the lowest stability (at a given IEC) of the two series upon submersing the membranes in water at 80 ^{o}C (Table 4-2).

Table 4-2. **Water stability data, including intrinsic viscosities before and after testing, for sulfonated polyimide copolymers as a function of structure and composition**

Membrane	Time Until Membrane Became Brittle (h)	Original IV (dL/g)*	IV After Test (dL/g)*
BAPS-00	1140[a]	1.17	1.12
BAPS-30	96	2.17	0.34
BAPS-40	66	2.19	0.27
BAPS-50	48	2.40	0.45
BAPS-60	42	2.51	0.38
BAPS-70	28	1.54	-
BAPS-80	18[b]	1.65	-
ODA-30	65	1.57	0.41
ODA-40	47	3.98	0.29
ODA-50	34	1.54	0.22
ODA-60	20	2.23	0.33
ODA-70	7[b]	1.04	-
ODA-80	0.5[b]	1.85	-

* pure NMP at 30 °C
[a] Membrane was still ductile after this time
[b] Membrane dissolved

4.4.5. Direct Methanol Fuel Cell (DMFC) Performance

The initial DMFC performance of Nafion 117, ODA-40, ODA-50 and ODA-60 at 80 ^{o}C is shown in Figures 4-6 and 4-7. It is important to note that the polarization curves were taken after one hour under DMFC conditions, before any copolymer hydrolysis had occurred. The performance of ODA-40 and ODA-60 copolyimides was comparable to that of Nafion 117, which has been extensively studied at Los Alamos National Laboratories (LANL) and elsewhere. ODA-60 performed slightly better than ODA-40, possibly due to the lower resistance in the ODA-60 membrane. It is interesting to note that the IECs of ODA-40 and ODA-60 are much higher than Nafion 117, but the overall performance of all three membranes was similar. This effect may be due to the large difference in both proton conductivity and methanol permeability of the membranes. Nafion displayed the highest methanol permeability of the copolymer membranes tested. In fact, the IECs of BAPS-30 and Nafion are very close (0.88 and 0.91, respectively), but the methanol permeability of Nafion is higher by two orders of magnitude. The methanol permeability data of selected disulfonated polyimide copolymers, and Nafion as a comparison, are shown in Table 4-3. The methanol permeability of the polyimide copolymers varies in a consistent manner with the IEC.

The polarization curve is affected by the fuel cell operating conditions. For example, changes in temperature and pressure can cause the curve to shift up or down and can change the value of the limiting current. The DMFC conditions used to test these copolymers were optimized for Nafion 117 at LANL. Since the polyimide copolymers have very different properties than Nafion (i.e. lower conductivity and methanol permeability at the same IEC), it was necessary to examine the performance of these copolymers under different conditions. In this study, the effect of methanol concentration feed at the anode on the DMFC performance was tested (Figure 4-7).

Polarization curves are typically split into three divisions: activation polarization, ohmic polarization, and concentration polarization. The open circuit voltage is the cell voltage when the current is zero. As the current begins to flow, the voltage drops due to the activation polarization.[190] The open circuit voltage correlates with the crossover of methanol through the MEA. Consequently, as more methanol diffuses through the membrane, the open circuit voltage decreases. Therefore one expects that higher methanol feed concentrations would result in lower open circuit voltages. The polarization curve then takes on the linear shape associated with the ohmic losses, and this region can be correlated to the conductivity (or resistance) of the MEA. Since all of the membranes in Figure 7 are the same thickness and composition, the slope of the curves around 0.1 A cm^{-2} are indistinguishable. However, at high current densities, restrictions to the flow of reactants to the reaction sites lead to limiting current density. As a result, at lower methanol feed concentrations, the fuel is being consumed which results in mass transfer losses.

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[190] Ellis, M.W. *Fuel Cells for Building Applications*; American Society of Heating, Refrigerating and Air-Conditioning Engineers, Inc. (ASHRAE): Atlanta, 2002.

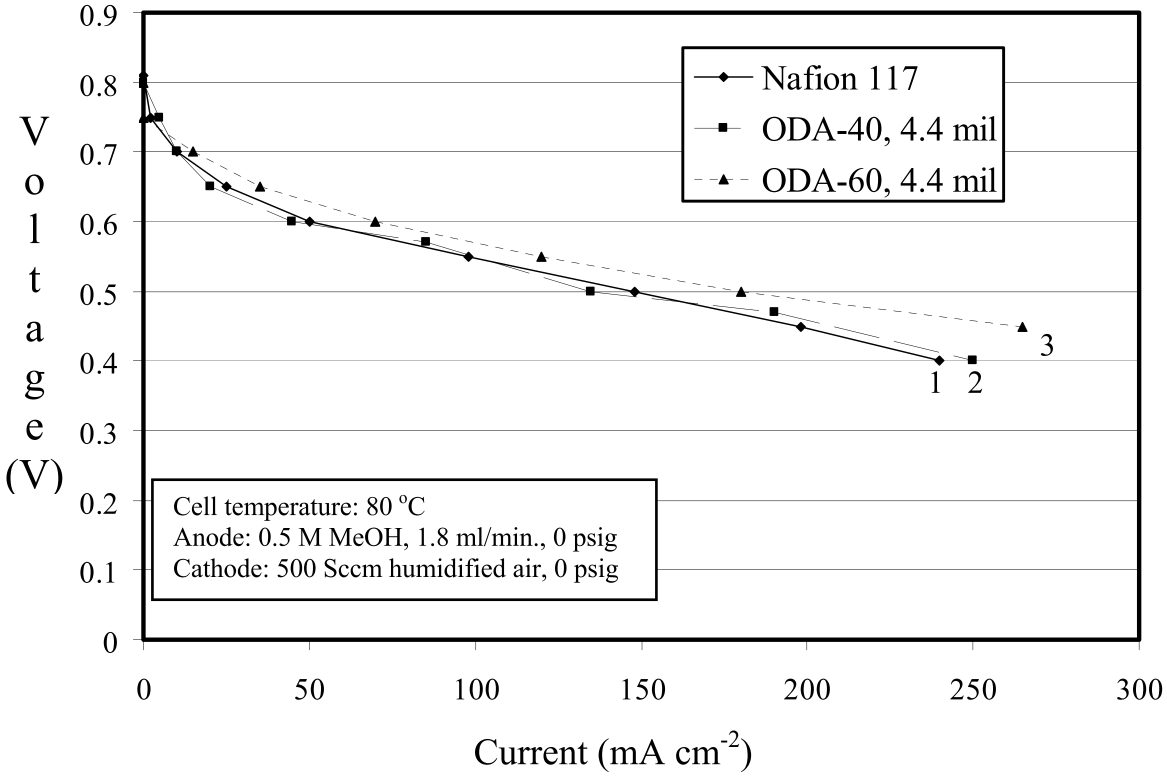

Figure 4-6. Initial direct methanol fuel cell performance data for Nafion 117, ODA-40 and ODA-60

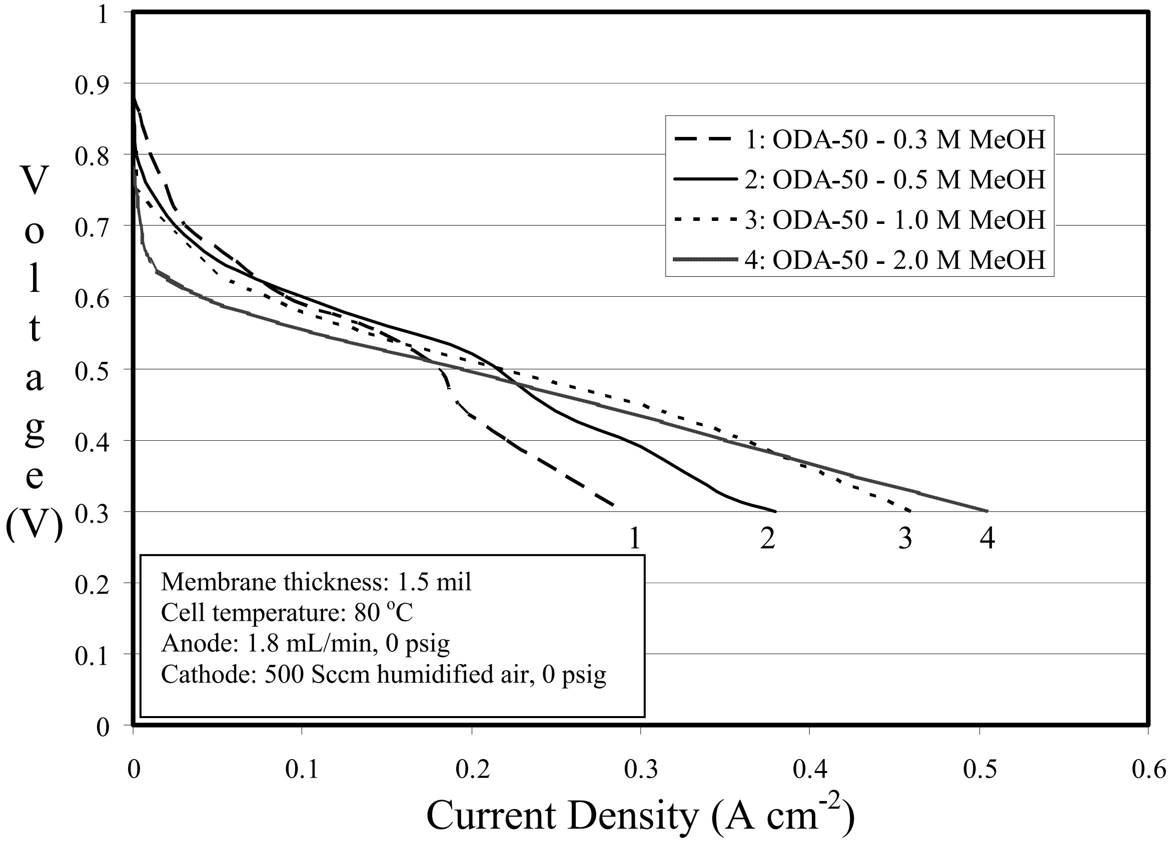

Figure 4-7. Effect of methanol concentration on the performance of ODA-50 copolyimide

Table 4-3. Methanol permeability of Nafion and selected polyimide copolymer membranes

Copolymer Membrane	IEC (meq g^{-1})	Methanol Permeability (cm^2 s^{-1})
BAPS-30	0.88	$6.6 * 10^{-8}$
BAPS-50	1.36	$3.3 * 10^{-7}$
BAPS-60	1.59	$4.5 * 10^{-7}$
BAPS-80	2.03	$8.0 * 10^{-7}$
ODA-30	1.09	$1.0 * 10^{-7}$
ODA-60	1.80	$5.1 * 10^{-7}$
ODA-70	1.98	$6.9 * 10^{-7}$
Nafion 117	0.91	$1.7 * 10^{-6}$

4.5. Conclusions

The effect of copolymer composition and ion exchange capacity on water sorption, proton conductivity and water stability at 80 °C was studied. The structure of the nonsulfonated diamine largely influenced the copolymer stability in water at 80 °C, but it had little effect on the proton conductivity and water sorption at comparable IECs. Relatively high proton conductivity values were achieved and were a function of temperature and relative humidity. The DMFC performance of several polyimide copolymer membranes indicates that these membranes have similar short-term performance to Nafion 117.

4.6 Acknowledgements

The authors would like to thank NASA Glenn (contract # NCC3-886) for their support of this research.

CHAPTER 5

SYNTHESIS AND CHARACTERIZATION OF DIRECTLY COPOLYMERIZED DISULFONATED POLYBENZOXAZOLE COPOLYMERS

Taken From:

Brian Einsla, Young Jun Kim, Charles Tchatchoua, James E. McGrath. Polybenzoxazoles for Use as Proton Exchange Membrane Fuel Cells. Abstracts of Papers, 204th National Meeting of the Electrochemical Society, Orlando, FL, October 12-16, 2003.

Brian R. Einsla, Young Jun Kim, Charles N. Tchatchoua, James E. McGrath. Disulfonated Polybenzoxazoles for Proton Exchange Membrane Fuel Cell Applications. *Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.)* **2003**, *44*, 645-646.

5.1. Abstract

The preparation of a series of disulfonated polybenzoxazoles from a novel sulfonated dicarboxylic acid monomer (SODBA) is discussed. The sulfonated aromatic diacid, SODBA, was used to prepare polybenzoxazole copolymers containing pendent sulfonic acid groups by a one-step high temperature polycondensation in polyphosphoric acid (PPA). High molecular weight film-forming statistical copolymers with controlled degrees of disulfonation were prepared by varying the stoichiometric ratio of sulfonated diacid (SODBA) to the nonsulfonated diacid (ODBA). Characterization by ^1H NMR,

FT-IR, IEC, and TGA demonstrated that SODBA was quantitatively incorporated into the copolymers. Solution-cast films of the sulfonated copolymers were prepared from N,N-dimethylacetamide and afforded tough, ductile membranes. The copolymerization in PPA generated copolymers in their sulfonic acid form, so there was no need for an additional acidification step. The water uptake and proton conductivity of the membranes increased with increasing degree of disulfonation, or ion exchange capacity. By increasing the temperature, the proton conductivity of the PBO membranes increased in both water and water vapor. The initial hydrogen/air fuel cell performance was tested for the 100% disulfonated PBO membrane. Although the performance was an improvement over Nafion 117 under the same conditions, the membrane quickly became brittle during testing. The instability of the polybenzoxazoles was attributed to the partial positive charge on the carbon of the heterocyclic ring.[191] The hydrolytic stability of the membranes was improved by the incorporation of electron-donating ether linkages, nevertheless the sulfonated copolymers became brittle after boiling in deionized water for one hour.

5.2. Introduction

Polybenzazoles are characterized by the heterocyclic functionality shown in Figure 5-1, where X = NH for polybenzimidazoles (PBI), X = O for polybenzoxazoles (PBO), and X = S for polybenzothiazoles (PBT). These polymers are typically synthesized from the reaction of dicarboxylic acids (or acid chlorides) with tetramines, bis(*o*-aminophenol)s, or bis(*o*-aminothiophenol)s, repectively. A broad range of

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[191] Kim, Y.J.; Einsla, B.R.; Tchatchoua, C.N.; McGrath, J.E. Synthesis of High Molecular Weight Polybenzoxazoles in Polyphosphoric Acid and Investigation of Their Hydrolytic Stability Under Acidic Conditions. *High Perf. Polym.* **2005**, *in press*.

synthetic routes have been developed in an attempt to facilitate easier and more cost-efficient methods of preparation. In the case of PBOs, several methods have been outlined to prepare the precursor poly(hydroxyamide), with subsequent cyclodehydration to the oxazole ring. In our own group, fluorinated PBOs were prepared by synthesizing the poly(hydroxyamide) at low temperature, and cyclization was achieved in solution in the presence of *o*-dichlorobenzene. A more common one-step synthetic procedure utilizing polyphosphoric acid (PPA) has also been shown to prepare high molecular weight polybenzazoles. PPA is a relatively inexpensive non-oxidizing medium that acts as the solvent, catalyst, and dehydrating agent in the polymerization.

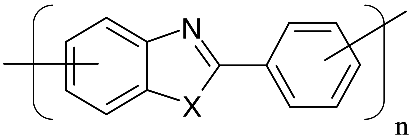

Figure 5-1. Chemical structure of polybenzazoles where X = NH for polybenzimidazoles, X = S for polybenzothiazoles and X = O for polybenzoxazoles

Polybenzoxazoles are known for their exceptional thermooxidative stability, high tensile modulus and strength, and superior hydrolytic stability.[192] Their excellent properties suggest that they could be good candidates for PEM fuel cells. To date, sulfonated polybenzoxazoles have not been widely studied. Sakaguchi et al. prepared

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[192] Wolfe, J.R. In *Encyclopedia of Polymer Science and Technology*; Mark, H.F.; Bikales, N.; Overberger, C.G.; Menges, G. Eds.; Wiley: New York, NY, 1988; Vol. 11, pp 601.

sulfonated PBOs and PBIs from 5-sulfoisophthalic acid and 2-sulfoterephthalic acid, though only the basic properties of the resulting copolymers were given.[193]

Herein, the synthesis and characterization of disulfonated polybenzoxazole copolymers is reported. The proton-conducting sulfonic acid sites were incorporated through a novel sulfonated diacid, SODBA. Film-forming PBOs were prepared from SODBA, 4,4'-oxydibenzoic acid (ODBA) and 2,2'-bis(3-amino-4-hydroxyphenyl)-hexafluoropropane (6FAP) using PPA as the polymerization media. The ratio of SODBA to ODBA was controlled to produce a series of copolymers from 0 to 100 % disulfonation. The membrane properties, including water uptake and conductivity, of these copolymers are described.

5.3. Experimental

5.3.1. Materials

4,4'-Hexafluoroisopropylidene diphenol (Bisphenol-AF) was kindly provided by Ciba and was used as received. 4,4'-Oxydibenzoic acid (ODBA), fuming sulfuric acid (30% free SO_3), concentrated nitric acid, acetic acid, palladium (5 wt.% on activated carbon), and phosphorus pentoxide were purchased from Aldrich and used without further purification. Hydrazine monohydrate was purchased from Acros. Polyphosphoric acid (PPA, 83% min.) was obtained from Fluka and was used as received.

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[193] Sakaguchi, Y.; Kitamura, K.; Nakao, J.; Hamamoto, S.; Tachimori, H.; Takase, S. Preparation and Properties of Sulfonated or Phosphonated Polybenzimidazoles and Polybenzoxazoles. *ACS Polym. Mat.: Sci. & Eng. (PMSE)* **2001**, *84*, 899-900.

5.3.2. 2,2'-Bis(3-nitro-4-hydroxyphenyl)-hexafluoropropane (6FNP)

In a typical reaction, 100 g of Bisphenol-AF and 500 mL of acetic acid were added to a 2 L 3-necked round-bottom flask equipped with a thermometer, reflux condenser and liquid addition funnel. The reaction mixture was cooled to 10 – 15 ^{o}C in an ice/water bath. Nitric acid/acetic acid solution (56 mL of 15.8 N nitric acid in 44 mL of acetic acid) was added dropwise from the addition funnel. The addition took place over a 2 h period and the temperature was maintained below 15 ^{o}C. After complete addition, the reaction was held at 15 ^{o}C for 1 h and 25 ^{o}C for 1 h. The reaction mixture was cooled to 10 ^{o}C and then added to 700 mL of deionized water to precipitate the product. The yellow product was filtered, washed with copious amounts of distilled water and dried under reduced pressure. Two recrystallizations from ethanol (one charcoal treatment) resulted in yellow needles.

5.3.3. 2,2'-Bis(3-amino-4-hydroxyphenyl)-hexafluoropropane (6FAP)

In a typical reaction, 100 g of 6FNP was charged to a 5 L 3-necked round-bottom flask with an overhead stirrer, an addition funnel and a reflux condenser. Absolute ethanol (1 L) was added and heated to about 50 ^{o}C under a rapid flow of nitrogen. A small amount of catalyst, Pd/C (~0.5 g) was introduced into the flask. Hydrazine monohydrate (9 times the stoichiometric amount) was introduced drop-wise by means of the addition funnel. No heat was needed at this stage because of the exothermic nature of the reaction. When the reaction decelerated as indicated by a reduction in the intensity of nitrogen evolution, more Pd/C (~0.5 g) catalyst was added to the reaction mixture and the system was heated to reflux for about 2 h. Decolorizing activated carbon (2 g) was then added to the reaction and a gentle reflux was allowed to continue for one additional hour. The dark solution was then cooled under nitrogen purge and subsequently filtered through celite with a Buchner funnel to afford a clear solution. The solution was added to deionized water and the product crystallized out overnight. The white solid was filtered and washed with copious amounts of deionized water. Purification procedure: To a 1 L 2-necked round-bottom flask with reflux condenser, mechanical stirrer and nitrogen purge, 100 g of crude 6FAP and 150 mL of 95% ethanol were combined and heated to reflux. Upon dissolution, ~150 mL of chloroform was added to the refluxing solution until turbidity was noticed. With continuous stirring, the solution was cooled and maintained at 25 °C for 2 h to allow for complete crystallization. The white crystals were filtered, washed with chloroform, and dried under vacuum at 100 °C for 24 h. The crude product could also be purified by vacuum sublimation. Pure 6FAP was dried under vacuum at 100 °C for at least 24 h before use.

5.3.4. Disodium-2,2'-disulfonate-4,4'-dicarboxydiphenyl ether (SODBA)

ODBA (28.7 g, 99 mmol) was dissolved in 60 mL of 30% fuming sulfuric acid (approximately a two-equivalent excess) in a 100-mL, three-necked flask equipped with a mechanical stirrer and nitrogen inlet/outlet. The reaction was heated to 110 °C for 2 h to produce a homogenous solution, cooled to room temperature, and dissolved into 400 mL of ice/water. Sodium chloride was added to produce a white precipitate identified as SODBA. The crude product was filtered and recrystallized from deionized water producing white crystals upon cooling over night. SODBA was dried under vacuum at 160 °C for at least 24 h before use. Yield: 98.3 % (45.0 g)

5.3.5. Polymer Synthesis

5.3.5.1. Synthesis of 6FAP/ODBA Control Polymer

In a typical polymerization, 83 g of 83% PPA and 11.5 g of P_2O_5 were charged to a 100 mL 3-necked round-bottom flask equipped with nitrogen inlet/outlet and mechanical stirrer. The mixture was stirred at 70 ^{o}C for about 20 minutes to incorporate the P_2O_5. Then 6FAP (0.7642 g, 4.6 mmol) and ODBA (1.1879 g, 4.6 mmol) were added and the temperature was kept at 70 ^{o}C overnight. The polymerization temperature was then slowly increased to 190 ^{o}C for 18 h, and then precipitated in deionized water in a blender. The polymer was filtered, stirred in 1 L of deionized water overnight, filtered again, and washed with deionized water. The polymer was dried at 120 ^{o}C under vacuum for 20 h.

5.3.5.2. Synthesis of 6FAP/SODBA/ODBA Copolymers

The polymerization method for a 50% disulfonated copolymer is given. In a typical polymerization, 83 g of 83% PPA and 11.5 g of P_2O_5 were charged to a 3-necked round-bottom flask equipped with nitrogen inlet/outlet and mechanical stirrer. The mixture was stirred at 70 ^{o}C for about 20 minutes to incorporate the P_2O_5. Then 6FAP (1.4650 g, 4 mmol), SODBA (0.9246 g, 2 mmol), and ODBA (0.5164 g, 2 mmol) were added and the temperature was kept at 70 ^{o}C overnight. The polymerization temperature was then slowly increased to 190 ^{o}C for 18 h, and then precipitated in deionized water in a blender. The sulfonated copolymer was filtered and washed with deionized water. Copolymers were dried at 120 ^{o}C under vacuum for 20 h.

5.3.6. Membrane preparation

1 g of copolymer was dissolved in 10 mL of dimethylacetamide (DMAc) and stirred overnight. The polymer solution was filtered through a Whatman 0.45 μm filter onto a clean, glass substrate. The solvent was evaporated at 35 ^{o}C under an IR lamp. Membranes were lifted off the glass plates by immersion in deionized water. All copolymer membranes were dried at 120 ^{o}C for 20 h.

5.3.7. Membrane Electrode Assembly Fabrication

Membrane electrode assemblies (MEAs) for all membranes were prepared with standard Nafion-based electrodes using a direct painting method developed at Los Alamos National Laboratory.[194] Catalyst loadings were approximately 6 mg/cm^2 of platinum black on the cathode, and 10 mg/cm^2 of platinum/ruthenium black on the anode.

5.3.8. Characterization

^{1}H NMR spectra were obtained on a Varian UNITY 400 MHz spectrometer operating at 399.952 MHz using DMSO-d6 as solvent. The thermo-oxidative behavior of the copolymers was performed on a TA Instruments TGA Q 500. Samples were pieces of thin films and totaled a weight of 10 to 15 mg. The samples were evaluated over the range of 30 to 800 ^{o}C at a heating rate of 10 ^{o}C/min in air. Due to the very low water uptakes of the copolymers, TGA was also utilized to determine water uptakes. After soaking the membrane in deionized water overnight, the membranes were quickly wiped dry and placed in the TGA furnace. The water uptake was determined by the weight loss

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[194] Thomas, S.C.; Ren, X.; Gottesfeld, S.; Zelenay, P. Direct Methanol Fuel Cells: Progress in Cell Performance and Cathode Research. *Electrochim. Acta* **2002**, *47*, 3741-3748.

at 200 °C and is presented as weight %. Conductivity measurements were performed on membranes after being soaked in deionized water for 3 days at room temperature. An impedance spectrum was recorded from 10 MHz to 10 Hz using a Hewlett-Packard 4129A Impedance/Gain-Phase Analyzer. The cell geometry was chosen to ensure that the membrane resistance dominated the response of the system. The resistance of the film was taken at the frequency which produced the minimum imaginary response. All impedance measurements were performed under fully hydrated conditions (30 °C in deionized water). The proton conductivity was taken as the reciprocal of the resistance and reported in units of Siemens per centimeter (S/cm). H_2/air fuel cell performance of the MEAs was tested using standard serpentine channel 5cm^2 Fuel Cell Technologies (Albuquerque, NM) fuel cell hardware with E-Tek (De Nora North America, Inc., Somerset, NJ) ELAT® gas diffusion backings. Hydrogen humidified to 15 °C above cell temperature was introduced to the cathode at a flowrate of 200 cm^3/min. Air humidified to 10 °C above cell temperature was introduced to the cathode at a flowrate of 500 cm^3/min. The anode and cathode cell outlets were maintained at 20 psig pressure. All tests were conducted at Los Alamos National Laboratory at an elevation of 7,500 feet above sea level.

5.4. Results and Discussion

Recent results have shown improved direct methanol fuel cell (DMFC) performance with fluorine-containing poly(arylene ether sulfone) copolymers.[195] It is believed that the fluorinated polymer backbone improves the adhesion between the

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[195] Kim, Y.S.; Pivovar, B. Direct Methanol Fuel Cell Performance and Properties of Sulfonated Poly(ether sulfone) Copolymers. *Abstracts of the 204th Electrochemical Society Meeting*, **2003**, *2003-02*, 1012.

membrane and the electrodes, which are composed of Nafion® 1100 perfluorosulfonic acid copolymer. Additional results have suggested that polymers with higher glass transition temperatures are needed for high temperature fuel cell operation. The hydrated T_g of Nafion 117 is ~90 °C and this may lead to its reduced performance above that temperature. Higher temperature operation (>120 °C) is desirable because it provides benefits such as faster electrode kinetics and greater tolerance to impurities in the fuel stream.[196] In 1994, Joseph et al. reported the T_g of a fluorine-containing polybenzoxazole to be ~280 °C.[197] Moreover, the polybenzoxazoles were good film-forming materials.[198] Therefore, the objectives of this work were to prepare similar polybenzoxazole copolymers that contained sulfonic acid groups to provide proton conductivity. The fluorinated backbone should improve the resulting membrane electrode assemblies for DMFCs, and the high T_g may allow for higher operating temperatures in hydrogen/air fuel cells.

To provide the polymer chain with fluorine atoms, 2,2'-Bis(3-amino-4-hydroxyphenyl)-hexafluoropropane (6FAP) was chosen as the bis(*o*-aminophenol). 6FAP was prepared by nitration of commercially available Bisphenol-AF and subsequent reduction with hydrazine in the presence of Pd/C (Figure 5-2). The nitrated Bisphenol-AF (6FNP) was purified by recrystallization in ethanol to produce bright yellow crystals. 6FAP could be purified by recrystallization in 1:1 ethanol:chloroform to provide fine

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[196] Alberti, G.; Casciola, M.; Massinelli, L.; Bauer, B. Polymeric Proton Conducting Membranes for Medium Temperature Fuel Cells (110-160 °C). *J. Membr. Sci.* **2001**, *185*, 73-81.

[197] Joseph, W.D.; Abed, J.C.; Mercier, R.; McGrath, J.E. Synthesis and Characterization of Fluorinated Polybenzoxazoles via Solution Cyclization Techniques. *Polymer* **1994**, *23*, 5046-5050.

[198] Joseph, W.D. Synthesis and Characterization of High Performance Polybenzoxazoles. Ph.D. Dissertation, Virginia Tech, Blacksburg, VA, 1993.

white crystals, but the yield was low. To improve the yield, crude 6FAP was sublimed under reduced pressure to obtain much higher yields of the monomer-grade bis(*o*-aminophenol).

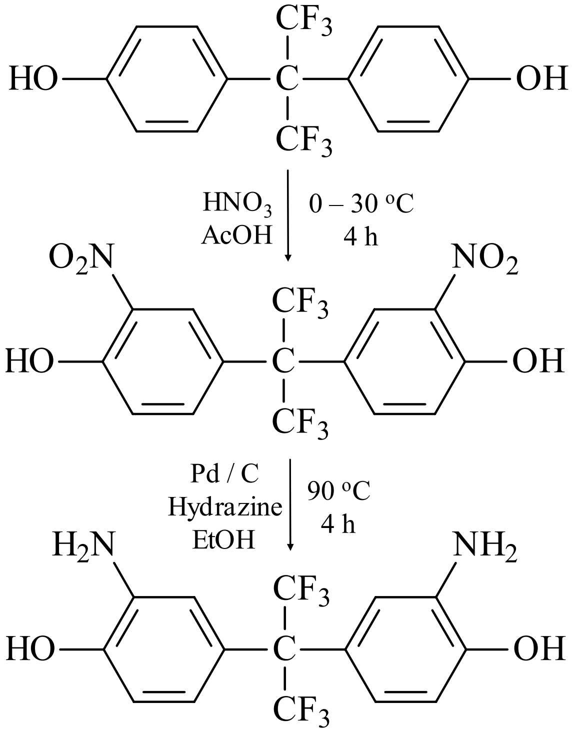

Figure 5-2. Synthesis of the fluorine-containing bis(*o*-aminophenol) 2,2'-bis(3-amino-4-hydroxyphenyl)-hexafluoropropane (6FAP)

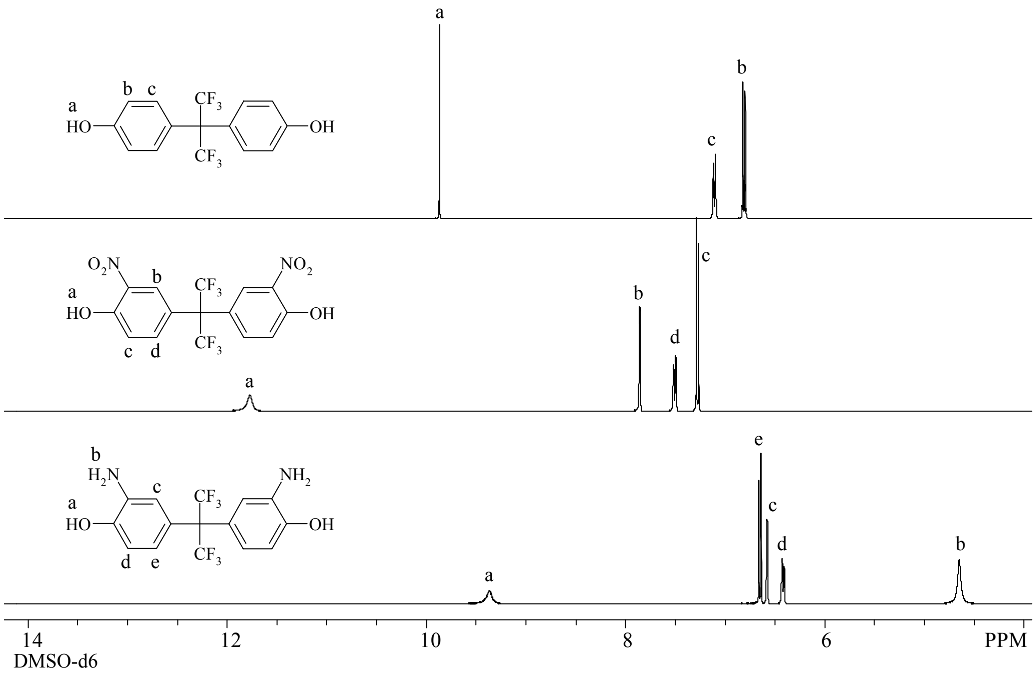

Figure 5-3. ^{1}H NMR of Bisphenol-AF (top), 6FNP (middle), and 6FAP (bottom)

The disulfonated monomer, SODBA, was prepared by direct sulfonation of 4,4'-oxydibenzoic acid (ODBA) in fuming sulfuric acid (Figure 5-4). Several sulfonated monomers have been prepared by this method, including SDCDPS in our own laboratory. A monomer more closely related to ODBA is 4,4,'-oxydianiline, where the carboxylic acid groups are replaced by amines. Okamoto et al. showed the sulfonation of 4,4,'-oxydianiline in fuming sulfuric acid.[199] The activated ether linkage allows for sulfonation *ortho* to the oxygen and *meta* to the amine (which is protonated in the sulfonation). Disulfonated monomers may allow for improved mechanical properties in the copolymer membrane. In the case of poly(arylene ether sulfone)s, copolymers with two sulfonic acid groups per repeat unit displayed lower water sorption than those with one sulfonic acid group per repeat unit, at similar IECs.[200]

Fuming sulfuric acid was added to ODBA under inert conditions and heated to 110 °C for 2 h. Upon cooling to room temperature, SODBA was obtained by adding the reaction mixture to ice water and then "salting out" the monomer with sodium chloride. Although the disulfonated monomer was pure at this time, it was necessary to recrystallize SODBA in deionized water to remove any remaining sodium chloride.

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[199] Fang, J.; Guo, X.; Harada, S.; Watari, T.; Tanaka, K.; Kita, H.; Okamoto, K.-I. Novel Sulfonated Polyimides as Polyelectrolytes for Fuel Cell Application. 1. Synthesis, Proton Conductivity, and Water Stability of Polyimides from 4,4'-Diaminodiphenyl Ether-2,2'-disulfonic Acid. *Macromolecules* **2002**, *35 (24)*, 9022-9028.

[200] McGrath, J.E.; Harrison, W.L.; Einsla, B.; Arnett, N.; Kim, Y.S.; Pivovar, B. Sulfonated Poly(arylene ether sulfone) as Candidates for Proton Exchange Membranes: Influence of Substitution Position on Membrane Properties. *Abstracts of the 204th Electrochemical Society Meeting*, **2004**, *2004-02*, 1973.

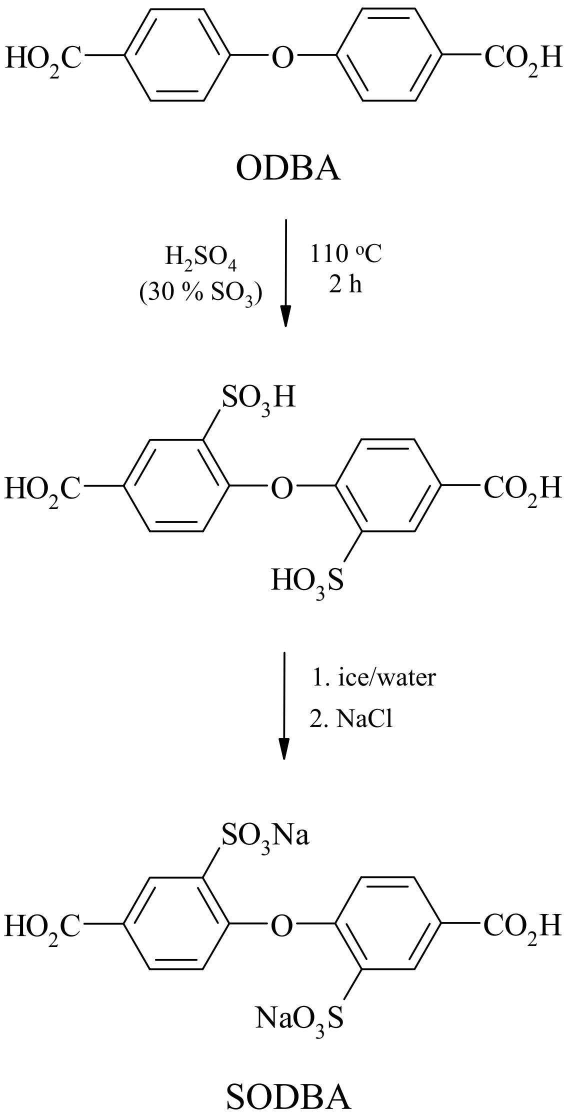

Figure 5-4. Direct sulfonation of 4,4'-oxydibenzoic acid (ODBA) to SODBA

The chemical structure of SODBA was confirmed by FT-IR, NMR and mass spectroscopy. The FT-IR spectra showed the stretching bands of the sodium sulfonate groups at 1034 cm^{-1} and the characteristic peaks of the carboxylic acid. The ^{1}H NMR spectrum displays four peaks at 13.0 ppm (broad), 8.4 ppm (s), 7.9 ppm (d), and 6.8 ppm (d) corresponding to the carboxylic acid and the aromatic hydrogens, respectively (Figure 5-5). The structural assignment is fairly straightforward. Since the molecule is symmetric, the hydrogens (and carbons) on either side of the ether bond are equivalent. Protons of carboxylic acid groups typically appear downfield and are broad due to hydrogen bonding. Therefore, the peak at 13.0 ppm is due to the proton of the carboxylic acid. The remaining resonances are in the aromatic region, so they correspond to the three protons of the phenyl ring. H_b is assigned to the peak at 8.4 ppm because (1) there are no adjacent hydrogens and it is the only singlet in the spectrum, and (2) it is the furthest downfield due to the electron-withdrawing carboxylic acid and sulfonate groups. The peaks at 7.9 ppm and 6.8 ppm are both doublets because protons H_c and H_d are on adjacent carbons. H_d is assigned to the peak at 6.8 ppm because it is further upfield due to the electron-donating ether linkage.

The ^{13}C NMR of SODBA displayed seven peaks corresponding to the six aromatic carbons and the one carboxylic acid (Figure 5-6). HSQC was used to help assign the remaining resonances in the ^{13}C NMR. Since the ^{1}H NMR assignments were already performed, HSQC can help assign the aromatic carbons with hydrogens attached (Figure 5-7).

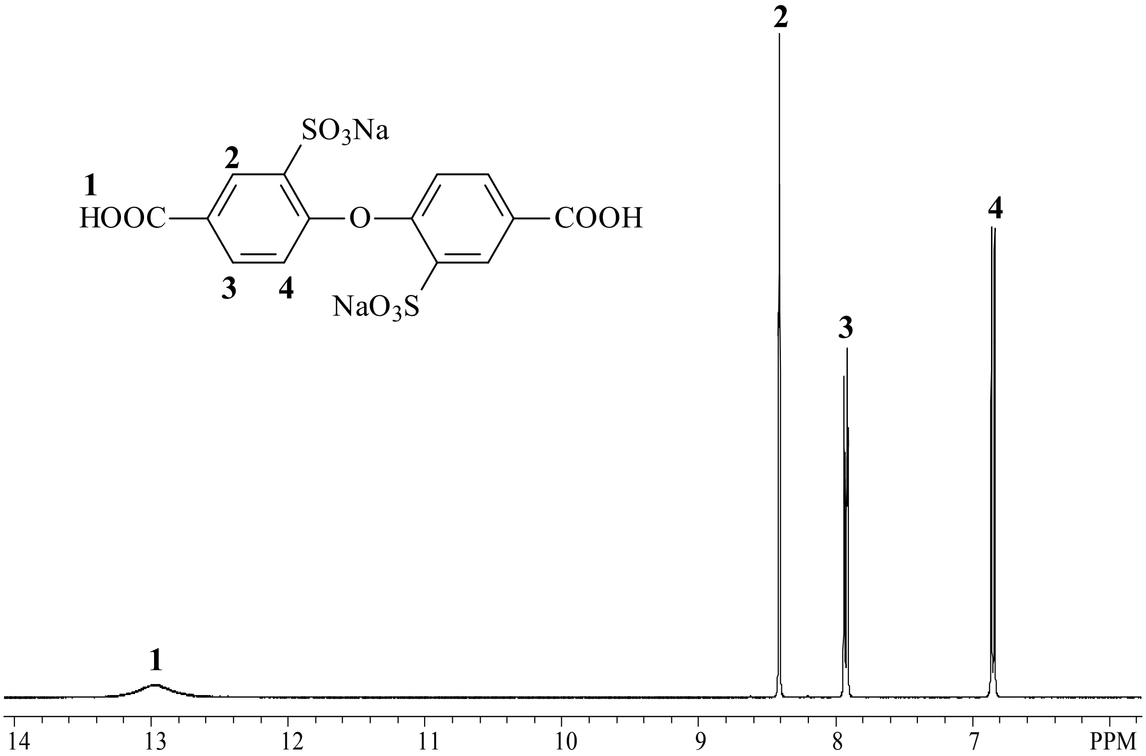

Figure 5-5. ^{1}H NMR and structural assignment of SODBA

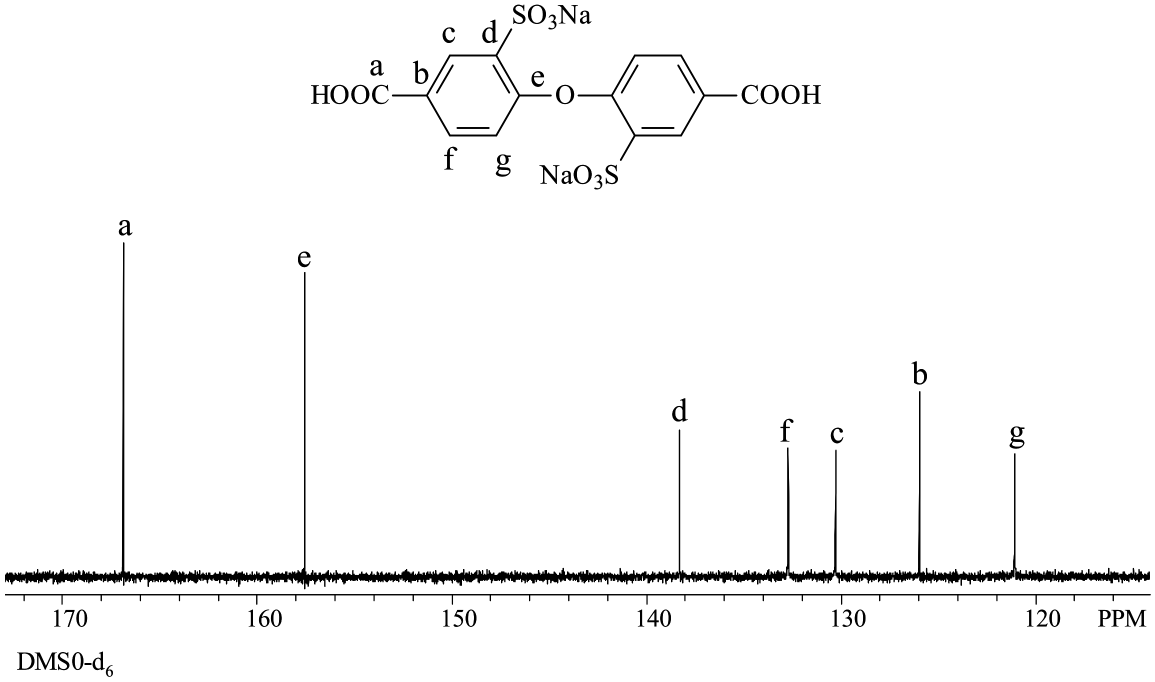

Figure 5-6. ^{13}C NMR and structural assignment of SODBA

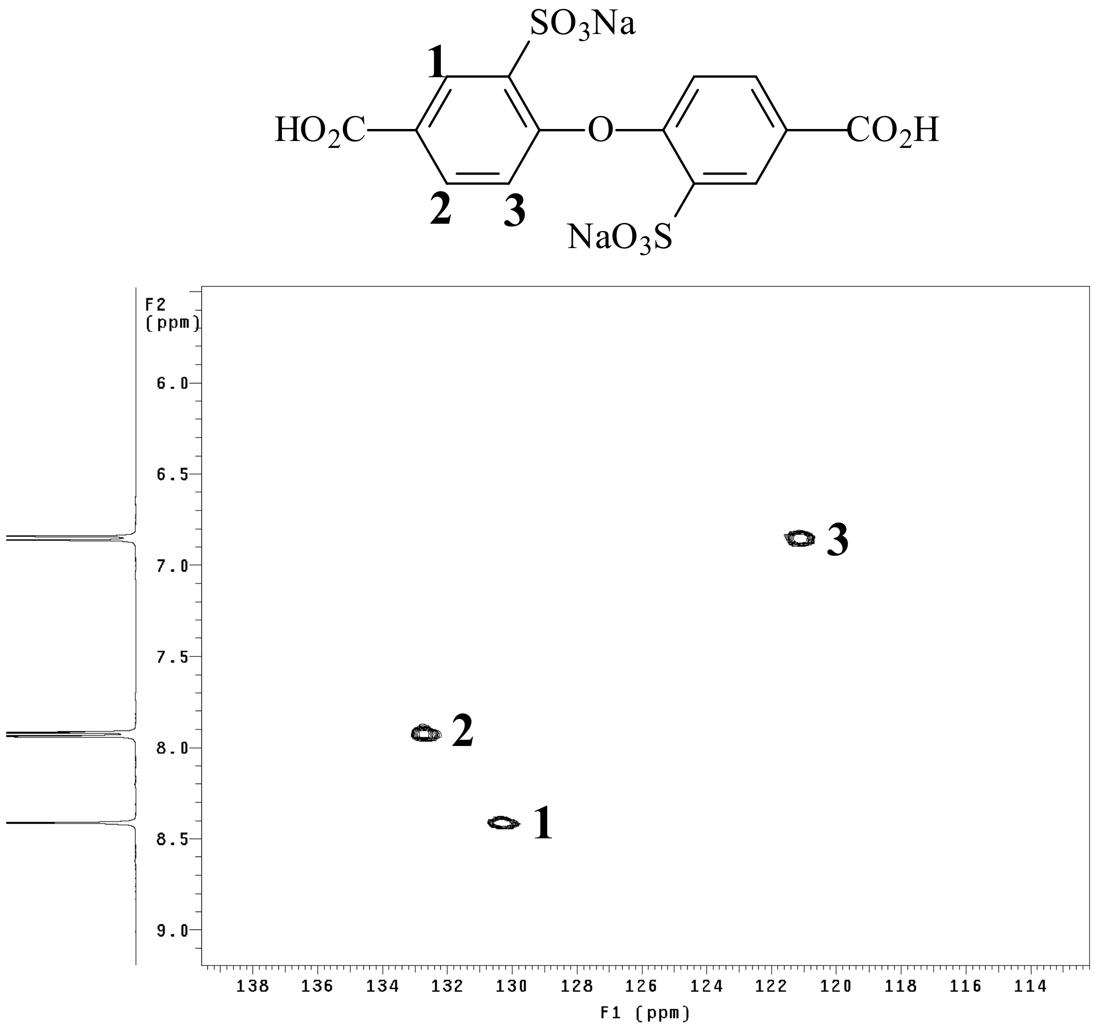

Figure 5-7. HSQC and assignment of SODBA

While there are many methods to prepare polybenzoxazoles, polymerization in PPA may be the most advantageous route for incorporation of sulfonated monomers. In the low temperature polymerization of poly(hydroxyamide)s followed by subsequent high temperature cyclization reactions, the acid chloride of the diacid is necessary to prepare high molecular weight materials. Refluxing in thionyl chloride converts the dicarboxylic acid to its reactive acid chloride. However, in a sulfonated monomer such as SODBA, thionyl chloride would also change the sulfonic acid groups to their sulfonyl chloride form.[201] Sulfonyl chlorides are unwanted in the polymerization because they are also reactive with the amine groups on the bis(*o*-aminophenol). This reaction would presumably convert the ionic sulfonated sites to reactive sites in the polymerization. Therefore, only reactions using the diacid of the monomer can be used for polymerization of PBOs.

For direct copolymerization of disulfonated PBOs, PPA has been advantageously employed as the reaction medium since it functions as a good reaction solvent, catalyst, and dehydrating agent. Copolymerizations were conducted in 85% polyphosphoric acid (PPA) under nitrogen. By increasing the relative concentration of phosphorus pentoxide in PPA from the commercially available 83% to 85%, higher molecular weight polymers were achieved. Polymerization of ODBA and 6FAP in 83% PPA led to an intrinsic viscosity (IV) of 0.82 dl/g and in 85% PPA the IV increased to 1.14 dl/g in methanesulfonic acid. In a typical polymerization, the reaction temperature was slowly increased to 190 °C, and then left at 190 °C for at least 18 h (Figure 5-8). The disulfonated PBO copolymers were isolated by adding the reaction mixture to deionized

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[201] Cho, C.G.; Hill, M.L.; McGrath, J.E. Synthesis and Characterization of Poly(arylene ether sulfone) Copolymers with Sulfonimide Side Groups. *ACS Div. Polym. Chem., Polym. Preprs.* **2003**, *44(2)*, 649-650.

water, filtering, and washing with deionized water until a neutral pH. This ensured the complete removal of any residual PPA.

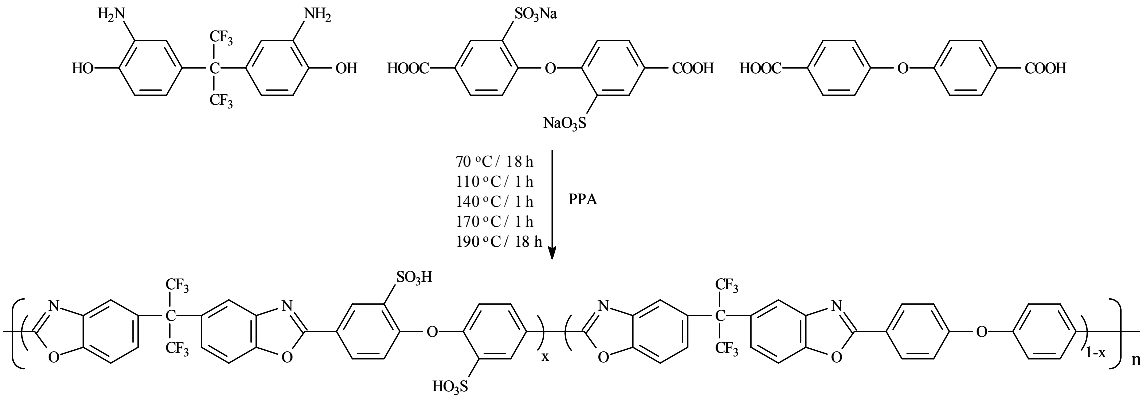

Figure 5-8. Direct copolymerization of disulfonated polybenzoxazole copolymers in polyphosphoric acid (PPA)

To ensure the polymerizations proceeded as expected, the incorporation of SODBA was examined by titration and ^{1}H NMR (Table 5-1). The ion exchange capacity (IEC), or milliequivalents of $-SO_3H$ per gram of polymer, was determined by titrating the copolymers with 0.01 N NaOH in the presence of sodium sulfate and deionized water. The sodium sulfate releases the protons of the sulfonic acid groups so they can be titrated with base. The experimental IEC was also determined by ^{1}H NMR. The proton adjacent to the sulfonic acid clearly resonates at 8.3 ppm. By taking the integration of this peak with respect to the sum of all the protons, the degree of disulfonation or IEC was calculated. The ion exchange capacities as determined by titration and ^{1}H NMR were in good agreement with the calculated values.

To prepare films, the dried sulfonated copolymers were dissolved in DMAc, filtered, and cast onto glass plates. After the solvent evaporated, the membranes were lifted from the glass plates by immersion in deionized water. The membranes were characterized by FT-IR, proton conductivity, and TGA for water uptake and thermal stability. The FT-IR clearly showed the stretching bands of the sodium sulfonate groups at 1034 cm^{-1} and the characteristic adsorption bands associated with the oxazole ring (1054 cm^{-1} for C-O stretch and 1616 cm^{-1} for C=N stretch).[202]

A TGA plot of the 40% and 60% disulfonated copolymers is shown in Figure 5-9. The membranes were placed in deionized water overnight, wiped dry and quickly placed in the TGA for analysis. The water uptake was determined as the weight loss at 200 ^{o}C since all of the water was removed and the temperature was below that for the loss of sulfonic acid groups (~250 ^{o}C). It was necessary to utilize TGA to determine the water

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[202] Hsaio, S.-H.; Chiou, J.-H. Aromatic Polybenzoxazoles Containing Ether-Sulfone Linkages. *J. Polymer Sci.: Part A: Polym. Chem.* **2001**, *39*, 2262-2270.

sorption values of these copolymers because absorption was so low. Traditional methods of weighing the dry and wet copolymers on a balance resulted in almost no change in weight. The water uptake values of the copolymers increased with increasing degree of disulfonation or ion exchange capacity (Table 5-1), which is consistent with other polymer systems.[203] The hydrophilic sulfonic acid groups readily absorb water, therefore by increasing the number of ionic sites the water uptake also increases. The TGA was also used to show the loss of sulfonic acid groups around 250 °C and polymer backbone degradation at about 500 °C. As shown in Table 5-1, the degradation temperature due to loss of sulfonic acid groups decreased from 288 °C to 251 °C as the degree of sulfonation increased.

The proton conductivity of the PBO copolymer membranes was measured at various temperatures (25 – 80 °C) in liquid water (Figure 5-10) and water vapor (Figure 5-11). At a given temperature, the conductivity of the copolymers increased with IEC. For a given copolymer, the conductivity increased with temperature. The proton conductivity values of the disulfonated PBOs were much lower than corresponding disulfonated poly(arylene ether)s and Nafion®. Even the 100% disulfonated PBO displayed lower proton conductivity values at 30 °C than Nafion®; 0.078 S/cm and 0.11 S/cm, respectively. In disulfonated poly(arylene ether sulfone) copolymer membranes, a hydrothermal boiling treatment was used to increase the proton conductivity and water uptake of the resulting copolymers.[203] This boiling treatment could be advantageous for these disulfonated PBOs because of their extremely low water uptake and relatively low

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[203] Kim, Y.S.; Wang, F.; Hickner, M.; McCartney, S.; Hong, Y.T.; Harrison, W.; Zawodzinski, T.A.; McGrath, J.E. Effect of Acidification Treatment and Morphological Stability of Sulfonated Poly(arylene ether sulfone) Copolymer Proton-Exchange Membranes for Fuel-Cell Use Above 100 °C. *J. Polym. Sci., Part B: Polym. Phys.* **2003**, *41*, 2816-2828.

proton conductivity values. After one hour in boiling water, all of the disulfonated PBO membranes became brittle and mechanically unstable.

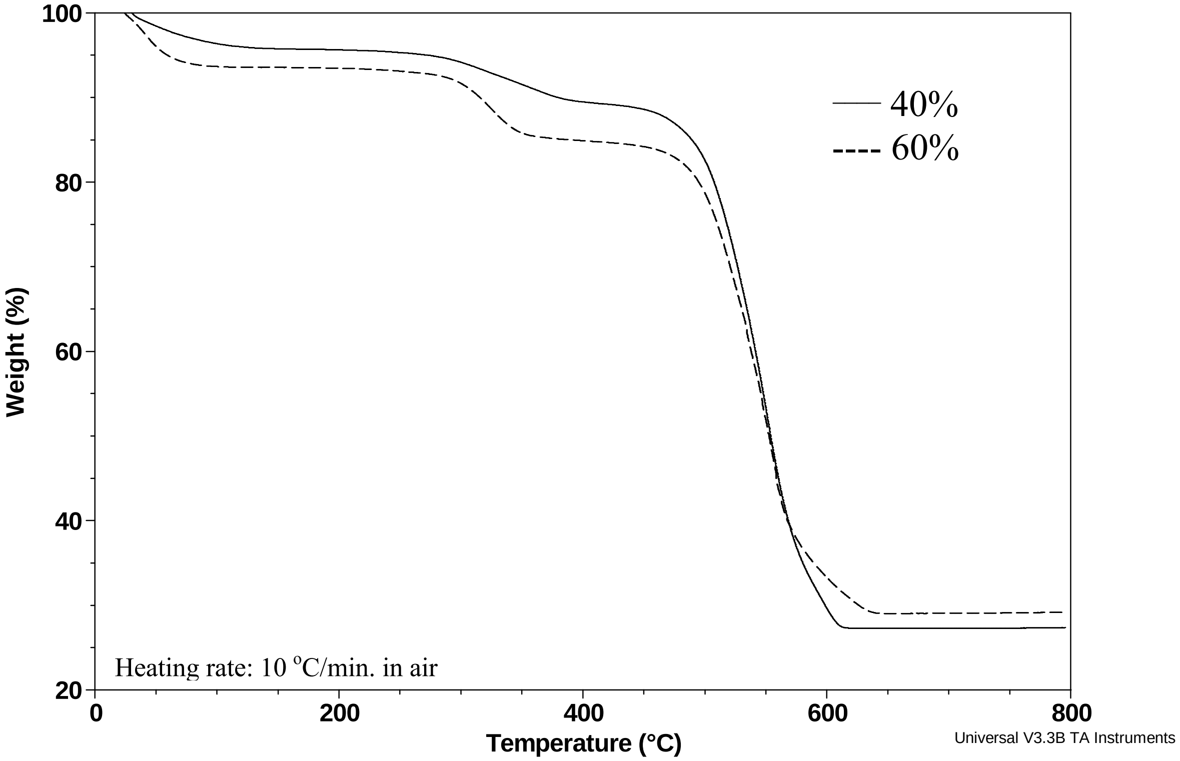

Figure 5-9. Thermogravimetric analysis (TGA) of the 40% and 60% disulfonated PBO copolymers for thermal stability and water sorption determination

Table 5-1. Selected Properties of disulfonated PBO copolymers

Copolymer	**Ion Exchange Capacity (meq/g)**			**Water Sorption (%)**	**T_d (^oC)**
	Calculated	Determined by Titration	Determined by ^{1}H NMR		
20	0.68	0.70	0.66	2.3	288
30	1.00	0.97	0.99	3.8	272
40	1.30	1.31	1.33	4.3	270
50	1.58	1.56	1.58	5.2	262
60	1.85	1.90	1.84	6.6	251
100	2.81	2.79	2.81	-	-

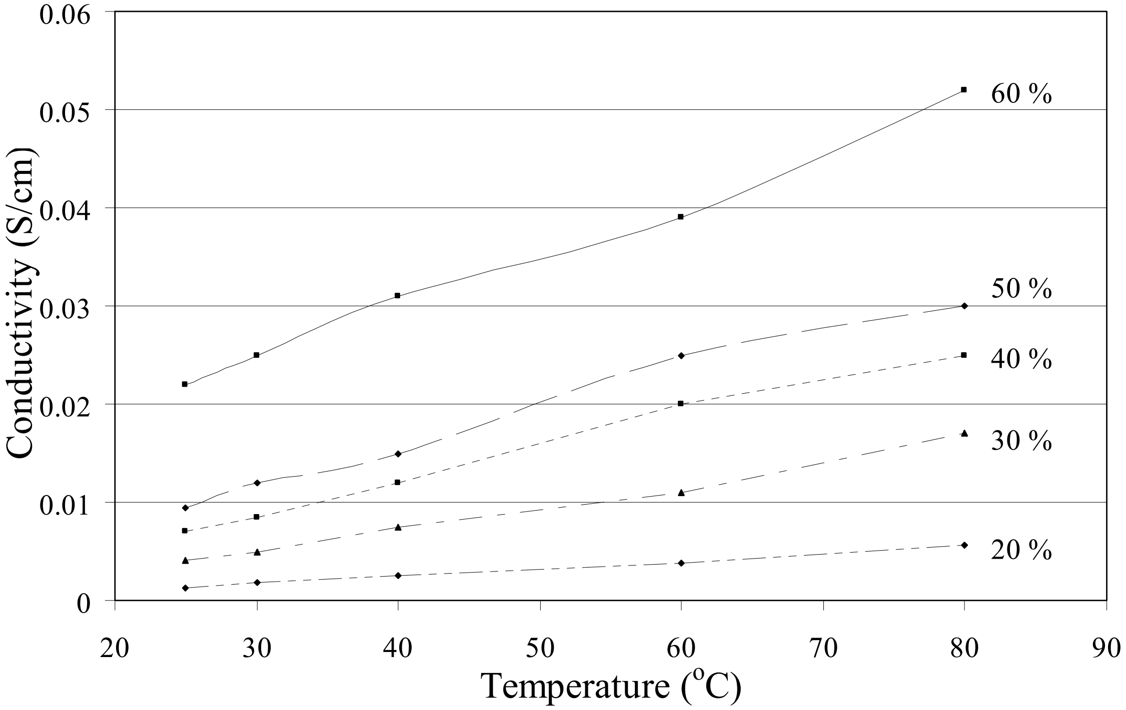

Figure 5-10. Effect of temperature and composition on the initial proton conductivity of disulfonated PBO copolymers in liquid water

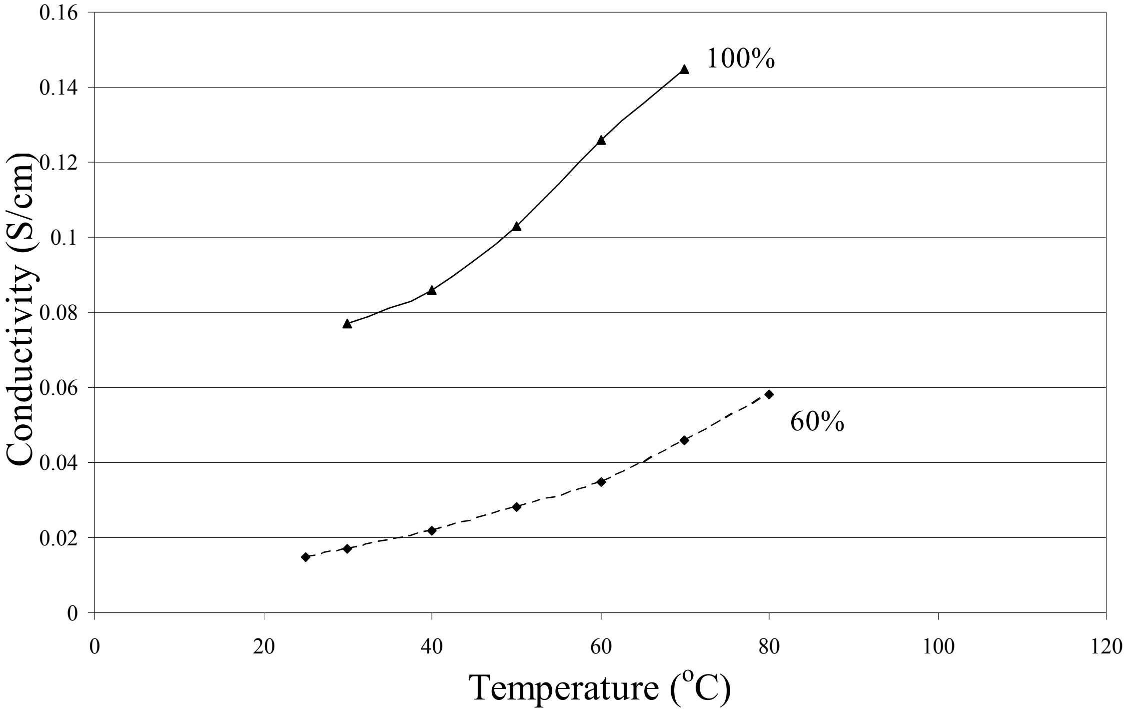

Figure 5-11. Effect of temperature on the proton conductivity at 100% relative humidity of the 60% and 100% disulfonated PBO copolymers

The H_2/air fuel cell performance of the 100% disulfonated PBO was studied due to its inherently high proton conductivity. The membrane electrode assembly (MEA) was prepared by painting the electrodes onto the PBO in a dispersion of Nafion® 1100. The MEA was placed into the fuel cell hardware, the flow of hydrogen and air were started, and the voltage of the cell was set to 0.5 V. The current density was measured as a function of time to show when the membrane failed (judged when the current density declined) (Figure 5-11). After 50 minutes under hydrated conditions and 25 minutes at 80 ^{o}C the current density started to rapidly decrease and the cell performance dropped. The cell was cooled to room temperature and disassembled to reveal that the MEA was brittle. The hydrolytic stability of nonsulfonated PBO copolymers was studied under very acidic conditions. The instability of the benzoxazole moiety was largely attributed to the partial positive charge associated to the carbon in the benzoxazole ring.[191]

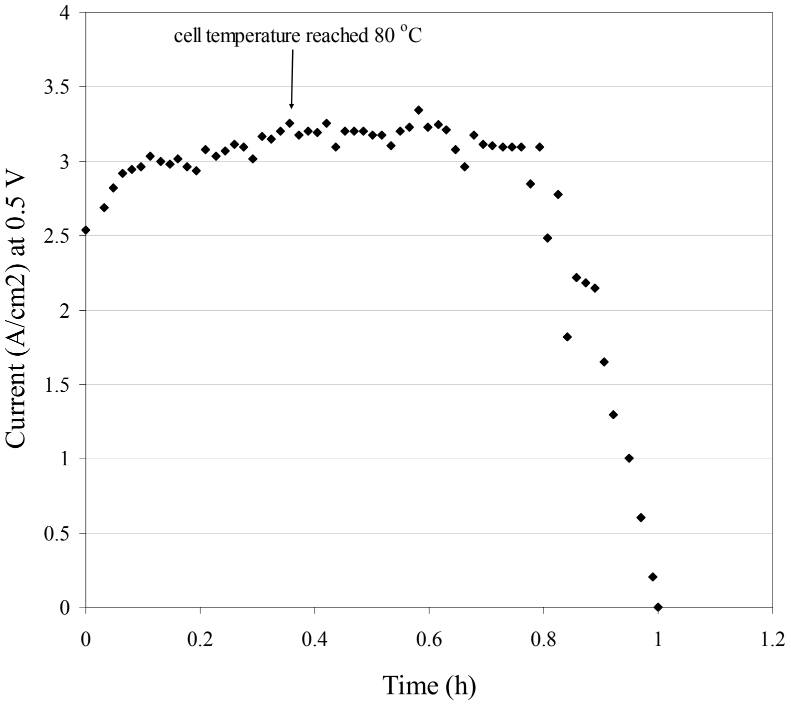

Figure 5-12. H_2/air fuel cell performance of 100% disulfonated PBO

5.5. Conclusions

A novel disulfonated monomer was synthesized by direct sulfonation of 4,4'-oxydibenzoic acid and characterized to confirm its structure. Film-forming PBO copolymers were prepared by a one-step high temperature polycondensation reaction in PPA. The copolymers were characterized by FTIR, proton conductivity, and TGA for water sorption and thermal stability. By increasing the IEC (incorporation of SODBA relative to ODBA), higher conductivities and water uptakes were achieved. The proton conductivity of the PBO membranes increased at elevated temperatures, but was low compared to other aromatic polymer systems studied in our group, i.e. polysulfones, polyimides. The lower conductivities may be a result of the much lower water uptake values of the PBO copolymers. Unfortunately, the sulfonic acid-containing PBOs quickly hydrolyzed.

5.6. Acknowledgements

The authors would like to thank NASA Glenn (contract # NCC3-886) for their support of this research.

CHAPTER 6

DIRECT COPOLYMERIZATION OF SULFONATED POLY(ARYLENE ETHER BENZIMIDAZOLE) COPOLYMERS FOR PROTON EXCHANGE MEMBRANE FUEL CELLS

Taken From:

Brian R. Einsla, Melinda L. Hill, William L. Harrison, Charles N. Tchatchoua, James E. McGrath. Direct Copolymerization of Sulfonated Poly(arylene ether benzimidazole) Copolymers for Proton Exchange Membrane Fuel Cells. *Proceeding of the 204th Electrochemical Society International Meeting* **2005**, *in press.*

6.1. Abstract

Polybenzimidazoles have largely been studied as candidates for proton exchange membrane fuel cells. A series of novel disulfonated poly(arylene ether benzimidazole)s was synthesized via nucleophilic aromatic polycondensation of disodium-3,3'-disulfonate-4,4'-dichlorodiphenylsulfone, dichlorodiphenylsulfone, and a benzimidazole-containing bisphenol (HPBI). The copolymers displayed inherently high intrinsic viscosities, due in part to the high molecular weights, but also because of the intermolecular association of the sulfonate groups. The structures (including the degree of disulfonation) of the copolymers were confirmed via ^{1}H NMR and FT-IR. Membranes were cast from the resulting copolymers which displayed lower water uptake and proton

conductivity compared to similar poly(arylene ether)s. Additionally, the thermal degradation of the sulfonate salt and sulfonic acid membranes was similar, suggesting an interaction between the sulfonic acid groups and the imidazole rings.

6.2. Introduction

Sulfonated poly(arylene ether sulfone)s are promising candidates for proton exchange membrane fuel cells.[204] In particular, wholly aromatic disulfonated poly(arylene ether sulfone) copolymers, BPSH, have a number of good properties compared to Nafion. In addition to BPSH, disulfonated poly(arylene ether ketone)s, thioether analogs, partially fluorinated systems, and nitrile or phosphine oxide-containing high performance PEMs have also been investigated. In particular, the nitrile-containing partially fluorinated copolymers (6FCN) have very good long-term DMFC performance due to their excellent compatibility with Nafion electrodes. Copolymers with basic moieties, such as nitriles and phosphine oxides, have interesting properties as a result of their interactions with the sulfonic acid groups on the copolymer chain.[205]

Polybenzimidazole (PBI) is a very basic polymer that has generated much attention as a candidate for proton exchange membrane fuel cells.[206] The basic nature of the imidazole ring promotes interactions with strong acids such as sulfuric acid and also

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[204] Hickner, M.A.; Ghassemi, H.; Kim, Y.S.; Einsla, B.R.; McGrath, J.E. Alternative Polymer Systems for Proton Exchange Membranes (PEMs). *Chem. Rev.* **2004**, *104*, 4587-4612.

[205] Kim, Y.S.; Pivovar, B.S. The Importance of Membrane-Electrode Interfaces on Long-Term Fuel Cell Performance. *Abstracts of Papers,* Advances in Materials for Proton Exchange Membrane Fuel Cell Systems 2005, Pacific Grove, CA, Feb 20-23, 2005; Preprint Number 35.

[206] Wainright, J.S.; Wang, J.-T.; Weng, D.; Savinell, R.F.; Litt, M. Acid-Doped Polybenzimidazoles: A New Polymer Electrolyte. *J. Electrochem. Soc.* **1995**, *142*, L121-L123.

phosphoric acid.[207,208] In particular, PBI can absorb significant amounts of phosphoric acid even from dilute aqueous solutions.[209] Recently, Benicewicz et al. described a novel method to load PBI membranes with high levels of phosphoric acid.[210] Polybenzimidazoles were prepared in polyphosphoric acid, directly cast from the polymerization solvent, and then the polyphosphoric acid was hydrolyzed to phosphoric acid in a sol-gel process. The resulting membranes showed inherently high proton conductivities even at low humidity, presumably due to the high acid doping levels.[211]

It has been shown that the conductivity of polybenzimidazole membranes could be improved by introduction of sulfonic acid sites. Sulfonated PBIs have been synthesized in various different methods, including post-sulfonation, direct copolymerization of sulfonated monomers, and grafting sulfonate groups to the PBI backbone. Post-sulfonation of PBI was accomplished by first doping with sulfuric acid, then heating the membrane to 200 °C. Direct copolymerization refers to the preparation of ionic polymers from monomers with proton conducting groups. This procedure allows for enhanced control of the degree of sulfonation. Direct copolymerization of sulfonated PBI was achieved using 5-sulfoisophthalic acid as the sulfonated monomer. The degree

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[207] Schuster, M.F.H.; Meyer, W.H. Anhydrous Proton-Conducting Polymers, *Annu. Rev. Mater. Res.* **2003**, *33*, 233-261.

[208] Bouchet, R.; Sieber, E. Proton Conduction in Acid Doped Polybenzimidazole. *Solid State Ionics* **1999**, *118*, 287-299.

[209] Glipa, X.; Bonnet, B.; Mula, B.; Jones, D.J.; Roziere, J. Investigation of the Conduction Properties of Phosphoric and Sulfuric Acid Doped Polybenzimidazole. *J. Mater. Chem.* **1999**, *9*, 3045-3049.

[210] Zhang, H.; Chen, R.; Ramanathan, L.S.; Scanlon, E.; Xiao, L.; Choe, E.-W.; Benicewicz, B.C. Synthesis, Characterization and Fuel Cell Performance of Poly(2,2'-(p-phenylene)-5,5'-bibenzimidazole) as a High Temperature Fuel Cell Membrane. *ACS Div. Fuel Chem. Preprs.* **2004**, *49*, 588-589.

[211] Xiao, L.; Zhang, H.; Choe, E,-W.; Scanlon, E.; Ramanathan, L.S.; Benicewicz, B.C. Synthesis and Characterization of Pyridine-Based Polybenzimidazoles as Novel Fuel Cell Membrane Materials. *ACS Div. Fuel Chem. Preprs.* **2003**, *48*, 447-448.

of sulfonation was varied to achieve copolymers with a range of ion exchange capacities. In all cases, the sulfonic acid sites coordinated with the benzimidazole ring to form a salt complex.

In the case of sulfonated poly(arylene ether sulfone)s, direct copolymerization leads to increased acidity of the proton-conducting sites, precise control of the ion exchange capacity, and improved thermal and mechanical stability.[212] The increased acidity of the sulfonic acid groups is attributed to their location adjacent to the sulfone moiety, which also leads to enhanced thermal stability. Our group has shown the direct synthesis of novel sulfonated poly(arylene ether)s from sulfonated monomers. The resulting copolymers have several improvements over the traditionally post-sulfonated materials. By incorporating two sulfonic acid sites per repeat unit (vs. one), the water uptake of the directly copolymerized materials is lower at comparable ion exchange capacities. This allows for improvements in mechanical stability and membrane electrode assembly durability.

Poly(arylene ether benzimidazole)s have been prepared via nucleophilic aromatic substitution of either a benzimidazole-containing bisphenol or an activated substituted difluoro benzimidazole. Heterocyclic functionalities, such as imides, benzoxazoles and benzimidazoles, are sufficiently electron withdrawing to activate aryl fluorides toward nucleophilic displacement. However, using such monomers would not produce benzimidazole units in each repeat unit since the sulfonated monomer is also an activated dihalide. Hergenrother et al. previously reported the synthesis of high molecular weight

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[212] Harrison, W.L.; O'Connor, K.; Arnett, N.; McGrath, J.E. Homogeneous Synthesis and Characterization of Sulfonated Poly(arylene ether sulfone)s Via Chlorosulfonic Acid. *ACS Div. Polym. Chem., Polym. Preprs.* **2002**, *43*, 1159.

poly(arylene ether benzimidazole)s from a novel benzimidazole-containing bisphenol.[213] Utilizing this bisphenol, along with disodium-3,3'-disulfonate-4,4'-dichlorodiphenylsulfone (S-DCDPS) and 4,4'-dichlorodiphenylsulfone (DCDPS), we report the synthesis and characterization of a systematic series of sulfonated poly(arylene ether sulfone benzimidazole) copolymers.

6.3. Experimental

6.3.1. Materials

4,4'-Dichlorodiphenyl sulfone (DCDPS) was kindly provided by Solvay Advanced Polymers. 3,3'-Diaminobenzidine was purchased from Aldrich and vacuum dried at 30 °C for 24 h before use. 4-Hydroxybenzoic acid phenyl ester was purchased from TCI and used as received. Potassium carbonate was purchased from Aldrich and vacuum dried at 120 °C for 24 h before use. N-Methylpyrrolidinone (Fisher) was distilled under reduced pressure over anhydrous P_2O_5 prior to use. N,N-Dimethylacetamide (DMAc) (Fisher) was used without further purification. Fuming sulfuric acid (27% SO_3), sodium chloride, phenylsulfone, isopropanol, toluene and concentrated sulfuric acid were used as received from Aldrich.

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[213] Hergenrother, P.M.; Smith Jr., J.G.; Connell, J.W. Synthesis and Properties of Poly(arylene ether benzimidazole)s. *Polymer* **1993**, *34*, 856-865.

6.3.2. Monomer Synthesis

6.3.2.1. Disodium-3,3'-disulfonate-4,4'-dichlorodiphenylsulfone (S-DCDPS)

The synthesis of S-DCDPS has been previously described.[214,215,216] In a typical reaction, DCDPS (28.7 g, 99 mmol) was dissolved in 60 mL (390 mmol SO_3) of fuming sulfuric acid (27% SO_3) in a 100-mL, three neck flask equipped with a mechanical stirrer, condenser, and a nitrogen inlet/outlet. The solution was heated to 110 ^oC for 6 hours to produce a homogeneous solution. The reaction was cooled to room temperature, dissolved into 400 mL of ice water, and 180 g of sodium chloride was added to produce a white precipitate of the product. The powder was filtered, redissolved in 400 mL of deionized water and neutralized to a pH ~ 6-7 with aqueous 2 N sodium hydroxide. An excess of sodium chloride (~180 g) was added to salt out the sodium form of the disulfonated monomer. The crude S-DCDPS was filtered and purified by recrystallization from a mixture of isopropanol and water (6/1, v/v). The resulting pure product was dried at 120 ^oC under vacuum for at least 24 hours. Yield 36.8 g (75%); ^1H NMR (400 MHz, DMSO-d_6) δ 8.33 ppm (d, 2H), 7.85 ppm (dd, 2H), 7.65 ppm (d, 2H); FT-IR (KBr) 1026 cm^{-1} (S=O, sulfonic acid, sym.), 1087 cm^{-1} (S=O sulfonic acid, asym.), 1168 cm^{-1} (S=O, sulfone); Mass Spectrum (FAB) 467 Daltons (S-DCDPS-Na^+);

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[214] Wang, F.; Hickner, M.; Ji, Q.; Harrison, W.; Mecham, J.; Zawodzinski, T.A.; McGrath, J.E. Synthesis of Highly Sulfonated Poly(arylene ether sulfone) Random (Statistical) Copolymers Via Direct Polymerization. *Macromol. Symp.* **2001**, *175*, 387-395.

[215] Harrison, W.L.; Wang, F.; Mecham, J.B.; Bhanu, V.A.; Hill, M.; Kim, Y.S.; McGrath, J.E. Influence of the Bisphenol Structure on the Direct Synthesis of Poly(arylene ether) Copolymers. I. *J. Polym. Sci:, Part A: Polym. Chem.* **2003**, 41, 2264-2276.

[216] Ueda, M.; Toyota, H.; Ochi, T.; Sugiyama, J.; Yonetake, K.; Mazuko, T.; Teremoto, T. Synthesis and Characterization of Aromatic Poly(ether sulfone)s Containing Pendent Sodium Sulfonate Groups. *J. Polym. Sci.: Polym. Chem. Ed.* **1993**, *31*, 853-858.

Elemental Analysis Calcd.: C, 27.3; H, 1.15; S, 18.2; Na, 8.72. Found: C, 27.4; H, 1.23; S, 19.3; Na, 9.36.

6.3.2.2. 5,5'-Bis[2-(4-hydroxyphenyl)benzimidazole] (HPBI)

The synthesis of HPBI has been previously described by Hergenrother et al. [213] In a typical reaction, 3,3'-diaminobenzidine (100 g, 0.467 mol), 4-hydroxybenzoic acid phenyl ester (200 g, 0.934 mol), phenyl sulfone (500 g) and toluene (150 mL) were added to a three-necked flask equipped with a mechanical stirrer, a Dean-Stark trap, a condenser, and a nitrogen inlet/outlet. The solution was allowed to reflux at 150 ^{o}C while water was azeotropically removed with toluene. After 7 h, the toluene was removed and the reaction temperature was increased to 280 ^{o}C for 2 h. Additional water and phenol generated during the reaction were removed via the Dean-Stark trap. At this point the product precipitated from solution. The temperature was increased to 300 ^{o}C and vacuum was applied to further remove the phenol generated in the reaction. After 3 h, the reaction was cooled to 150 ^{o}C and added to excess ethanol. After 12 h at room temperature, the phenylsulfone crystallized out of solution and was subsequently filtered off. The pure product was obtained by rotary evaporation and washing with excess acetone (2x). HPBI was dried at 120 ^{o}C under vacuum for at least 24 h. Yield: 90%. ^{1}H NMR (400 MHz, DMSO-d_6, δ): 12.72 (s, 2H), 10.00 (s, 2H), 8.05 (d, 4H), 7.79 (s, 2H), 7.64 (d, 2H), 7.52 (d, 2H), 6.95 (d, 4H).

6.3.3. Synthesis of Disulfonated Poly(arylene ether sulfone benzimidazole) Copolymers

The direct synthesis of a disulfonated poly(arylene ether sulfone benzimidazole) with 50 mol % disulfonation is discussed. DCDPS (2.000 g, 7 mmol), SDCDPS (3.4210 g, 7 mmol), and HPBI (5.8286 g, 14 mmol) were introduced into a 250-mL, three-necked flask equipped with a mechanical stirrer, a Dean-Stark trap, a condenser, and a nitrogen inlet/outlet. Potassium carbonate (2.21 g) and 75 mL of NMP were added to the reaction flask to afford a 15% (w/v) solid concentration. Toluene (40 mL) was added to the flask as an azeotroping agent. The Dean-Stark trap was filled with toluene and the reaction mixture was heated to 140 ^{o}C to dehydrate the system. After 4 h at 140 ^{o}C, the Dean-Stark trap was emptied and the oil bath temperature was heated to 190 ^{o}C (170 ^{o}C internal reaction temperature) for 20 h. The resulting viscous solution was diluted with DMAc, cooled to room temperature, and precipitated into an excess of deionized water. The precipitated copolymer was collected by filtration and the resulting yellow, fibrous copolymer was dried under vacuum at 120 ^{o}C for at least 24 h.

6.3.4. Membrane Preparation

Membranes were prepared by first dissolving the copolymers in DMAc at 50 ^{o}C. After filtering through a 0.45-μm Teflon membrane filter, the solution was cast directly onto a glass plate. The solvent was evaporated under nitrogen flow at 40 ^{o}C. The membranes were removed from the glass substrates by submersion in deionized water and then vacuum-dried at 120 ^{o}C for 24 h. The copolymer membranes were converted to their acid form by immersion in boiling 0.5 M H_2SO_4 for 2 h followed by boiling deionized water for 2h. All of the membranes were soaked in room temperature deionized water for 48 h before testing. In all cases, tough, ductile, transparent-yellow membranes were obtained.

6.4. Results and Discussion

As with any type of step-growth (condensation) polymerization, monomer purity is essential. 5,5'-Bis[2-(4-hydroxyphenyl)benzimidazole] (HPBI) has been previously prepared where the tetraamine is reacted with the phenyl ester of the carboxylic acid in phenyl sulfone (Figure 6-1).[213] The procedure used herein was identical to that reported by Hergenrother et al., with the exception of one additional step. The reaction mixture was first added to ethanol to crystallize the phenylsulfone and remove it (by filtration) from the product. Pure HPBI was obtained by rotary evaporation and washing twice with acetone. This provided highly pure HPBI, as determined by ^{1}H NMR (Figure 6-2).

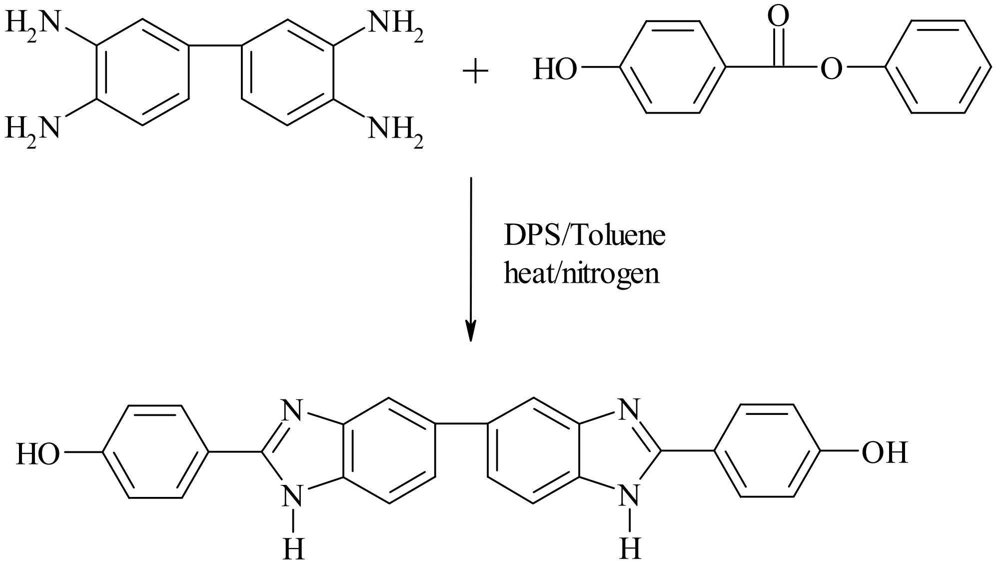

Figure 6-1. Synthesis of Benzimidazole-Bisphenol HPBI[213]

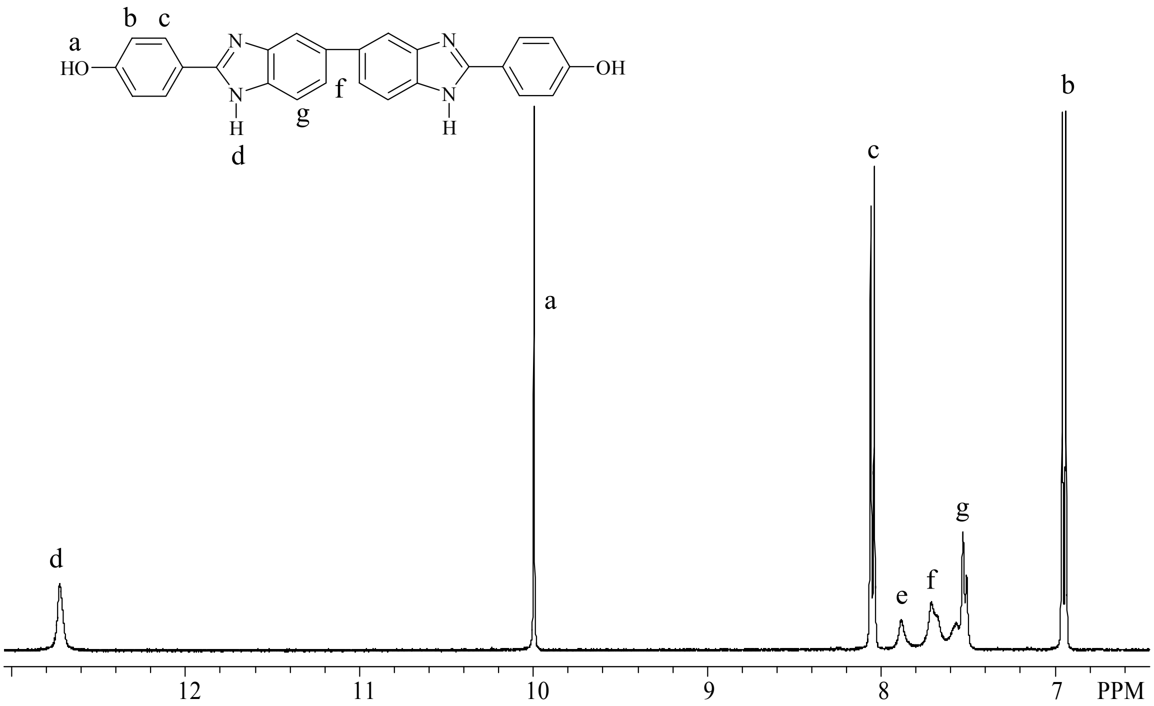

Figure 6-2. ^{1}H NMR of HPBI (DMSO-d_6)

Poly(arylene ether)s are most commonly synthesized via nucleophilic aromatic substitution of an activated dihalide with the bis-phenate of an aromatic bisphenol.[217] Nucleophilic aromatic substitution reactions are typically performed in high boiling polar aprotic solvents in the presence of base. Potassium carbonate was used in the copolymerizations to convert the benzimidazole bisphenol, HPBI, to the more reactive anion with no hydrolytic side reactions.[217] Hergenrother et al. synthesized the control polymer using 4,4'-difluorodiphenylsulfone and HPBI in DMAc at 160 °C. In this study, it was advantageous to use the slightly less reactive dichloride monomers in order to reduce the cost. To obtain high molecular weight polymers from 4,4'-dichlorodiphenylsulfone, higher reaction temperatures were required. Therefore, N-methylpyrrolidinone was chosen as the solvent because it effectively solvated both the monomers and polymers, and allowed higher reaction temperatures (190 °C). Although NMP slowly undergoes ring opening (observable as a darkening of the solvent) when exposed to high temperatures in the presence of bases, and analogous decompositions are less frequent with DMAc, NMP was required to achieve the higher reaction temperatures as the boiling point of DMAc is 165 °C.

High molecular weight sulfonated poly(arylene ether)s based on HPBI were successfully synthesized via nucleophilic aromatic substitution (Figure 6-3). High reaction temperatures were necessary as a consequence of the deactivating effect of the benzimidazole moiety in the bisphenol monomer and the steric hindrance of the sulfonate groups in disodium-3,3'-disulfonate-4,4'-dichlorodiphenylsulfone (S-DCDPS). Nevertheless, the high reaction temperatures are consistent with previous direct

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[217] Viswanathan, R.; Johnson, B.C.; McGrath, J.E. Synthesis, Kinetic Observations and Characteristics of Polyarylene Ether Sulphones Prepared via a Potassium Carbonated DMAC Process. *Polymer* **1984**, *25*, 1827-1836.

copolymerization procedures of sulfonated poly(arylene ether)s. The degree of disulfonation (or ion exchange capacity) was easily controlled by varying the ratio of SDCDPS to DCDPS in the reaction. Sulfonated copolymers were prepared with degrees of disulfonation ranging from 0 to 50% and IECs from 0 to 1.40 meq/g. The benzimidazole bisphenol, HPBI, was chosen to study the effect of the incorporation of benzimidazole units on the properties of the resulting copolymers. The copolymerizations were complete after 24 hours as evidenced by the high viscosity. The copolymers had to be diluted with DMAc so the solutions could be poured from the flask and precipitated. In all cases, the copolymers produced tough, ductile membranes by solution casting from DMAc. The good film-formation and high intrinsic viscosity (IV) values ranging from 1.9 to 2.7 dL/g suggested that the polymers were high molecular weight. The extraordinarily high IV values are a result of intermolecular association and are not a reflection of absolute molecular weight. However, dilute solution viscometry is a good qualitative tool to establish the film-forming capability of resulting membranes.

^{1}H NMR was used to identify the molecular structure of the sulfonated copolymers and evaluate the degree of disulfonation (Figure 6-4). The degree of disulfonation was determined from the ratio of a peak in the sulfonated region to one in both the sulfonated and nonsulfonated regions. It has previously been shown that the resonance at 8.4 ppm is consistent with the protons adjacent to the sulfonate groups.[215] Since the benzimidazole units are within each repeat unit, the protons next to the carbon of the imidazole moiety were chosen as a reference. Using the equation in Figure 6-4, the experimental degrees of disulfonation were obtained from ^{1}H NMR. The values from ^{1}H

NMR agree with the feed ratios indicating that the incorporation of the sulfonated comonomer was quantitative (Table 6-1).

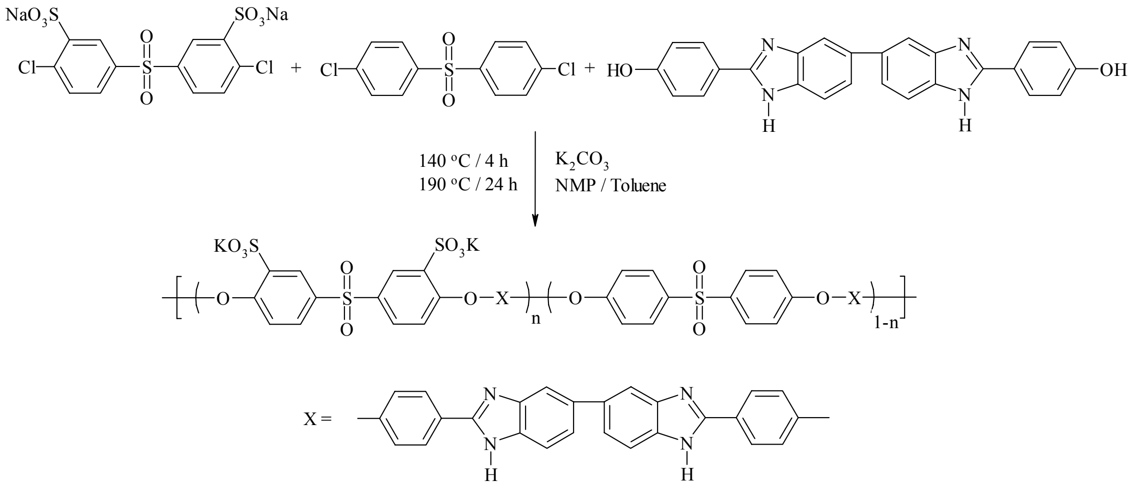
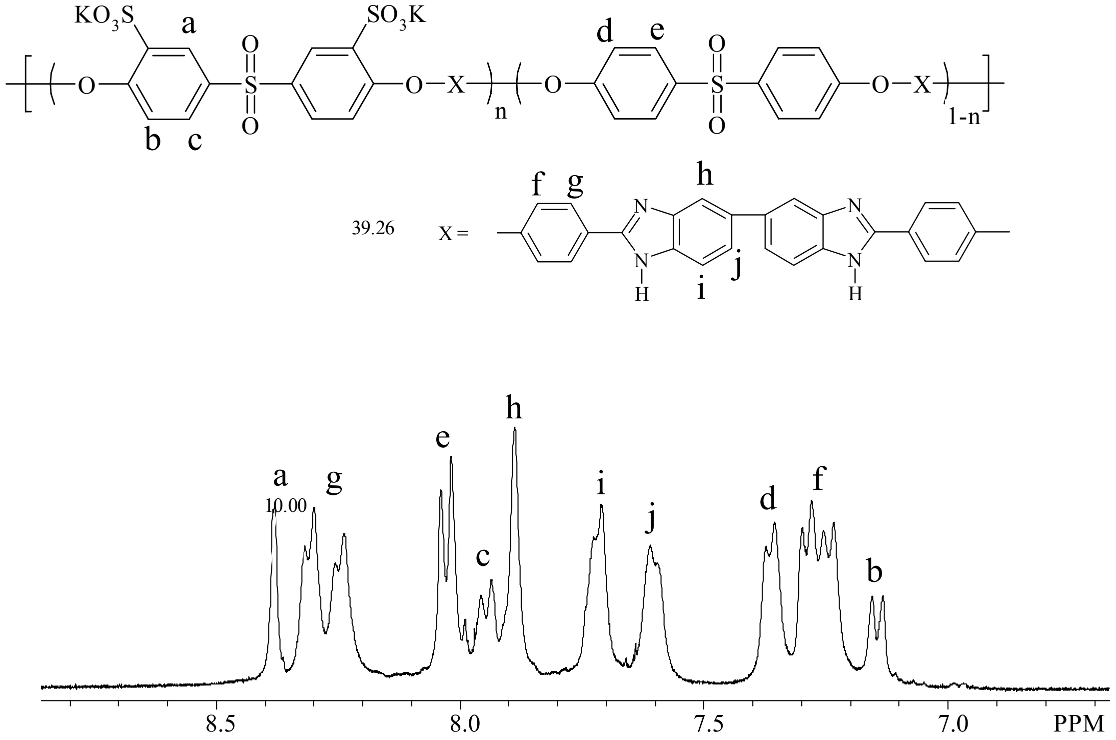


Figure 6-3. Direct copolymerization of disulfonated poly(arylene ether benzimidazole)s



$$\text{Degree of Disulfonation} = (2\ a / g) \cdot 100\%$$

$$= 2 \cdot (10.00 / 39.26) \cdot 100\% = 50.9\ \%$$

Figure 6-4. Determination of the degree of disulfonation and copolymer structure via ^{1}H NMR

Table 6-1. Selected Properties of disulfonated poly(arylene ether benzimidazole) copolymers

Copolymer Composition	IEC (meq g^{-1})	IV* (dL g^{-1})	Gel Permeation Chromatography** (g mol^{-1})			
			M_n	M_w	M_z	Polydispersity
0	0	1.62	33,400	239,000	1,590,000	7.2
10	0.31	2.55	40,100	300,000	1,646,000	7.5
20	0.60	2.29	29,500	100,000	570,000	3.4
30	0.88	2.75	50,500	363,000	1,784,000	7.2
40	1.15	1.86	35,200	294,000	1,809,000	8.4
50	1.40	1.94	36,800	231,000	1,446,000	6.3

[*] NMP at 25 °C

[**] GPC compared to polystyrene standards

Standardized FT-IR spectra allowed for determination of the functional groups in the copolymers. The spectra displayed the benzimidazole adsorption bands at 1716, 1678, and 1349 cm^{-1}, as well as those associated with the sulfonic acid groups (Figure 6-5). The symmetric and asymmetric stretches of the sulfonate groups appeared at 1030 and 1097 cm^{-1}, respectively. The intensities of the peaks at 1030 and 1097 cm^{-1} increased with the degree of disulfonation (Figure 6-6).

The thermal degradation behavior of the disulfonated copolymers in both their sulfonate salt and acid forms was investigated by TGA (Figure 6-7). The membranes were analyzed between 30 and 800 ^{o}C at a heating rate of 10 ^{o}C / min in air. A two-step degradation profile was observed for all disulfonated copolymers. The TGA profile of the acid form membranes was very similar to the potassium salt form. Typically, sulfonated poly(arylene ether)s degrade at about 250 ^{o}C for the sulfonic acid form and at about 400 ^{o}C for the potassium salt form. The five percent weight loss temperatures of the disulfonated benzimidazoles were far higher than most sulfonated poly(arylene ether)s, suggesting a strong interaction between the sulfonate groups and the imidazole ring.

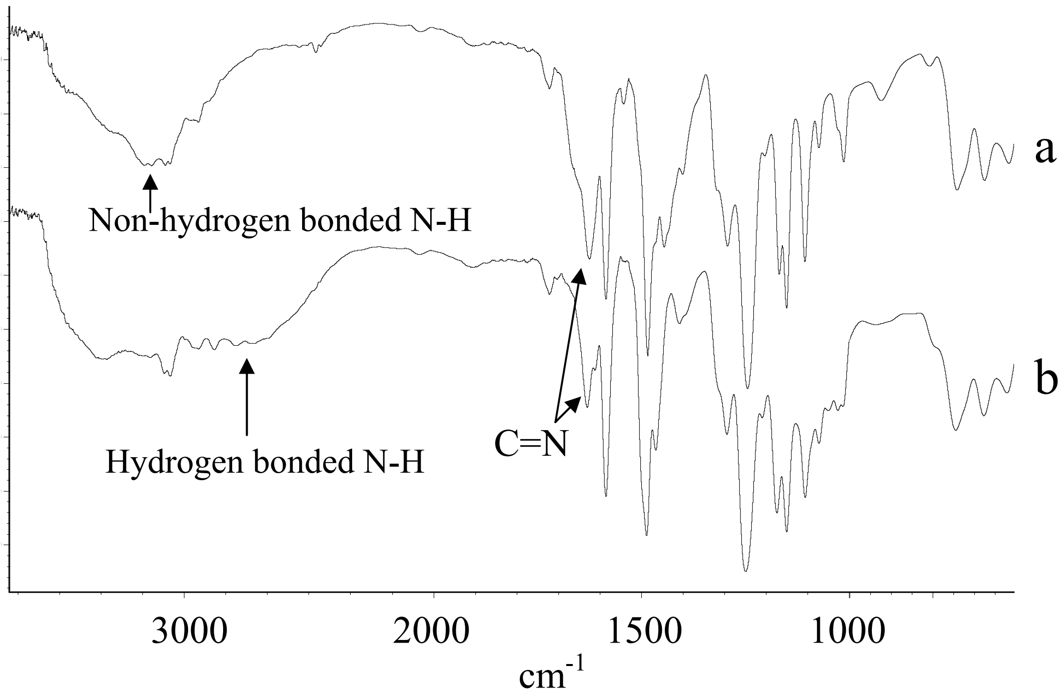


Figure 6-5. Transmission FT-IR of the (a) potassium salt form and (b) sulfonic acid form of the 10% disulfonated copolymer

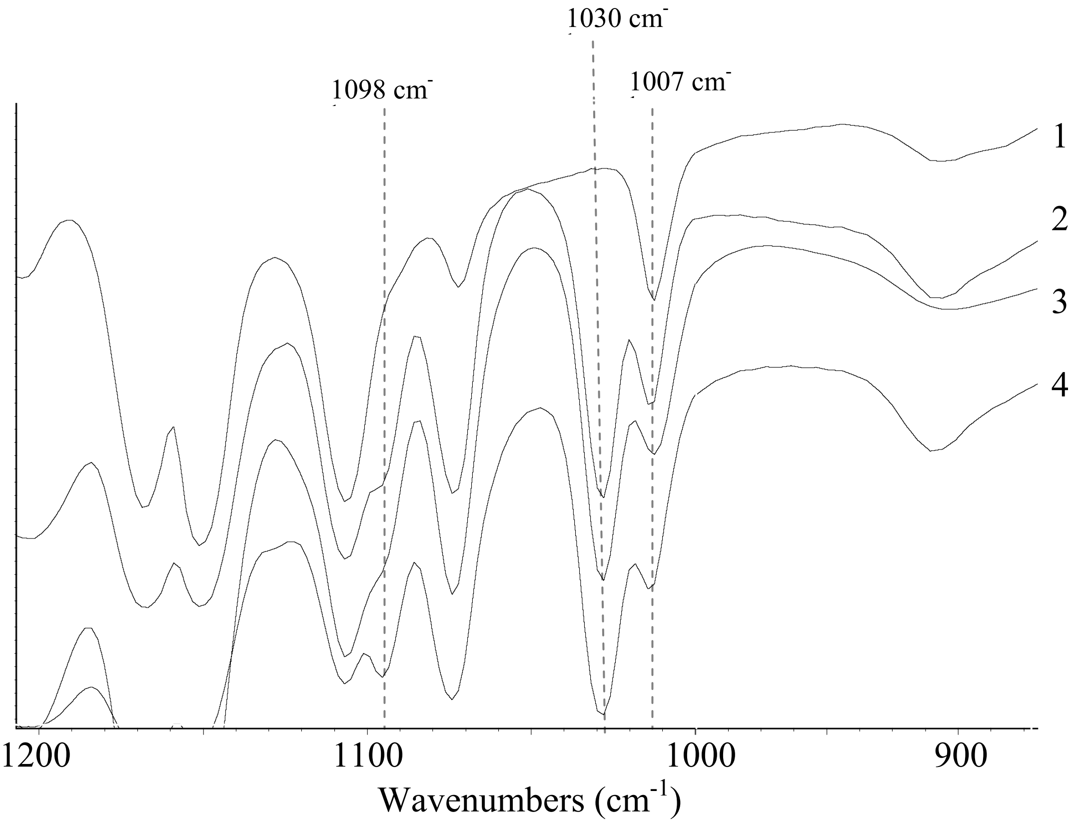


Figure 6-6. Transmission FT-IR of (1) 0 %, (2) 20 %, (3) 40 %, and (4) 50 % disulfonated polybenzimidazole copolymers

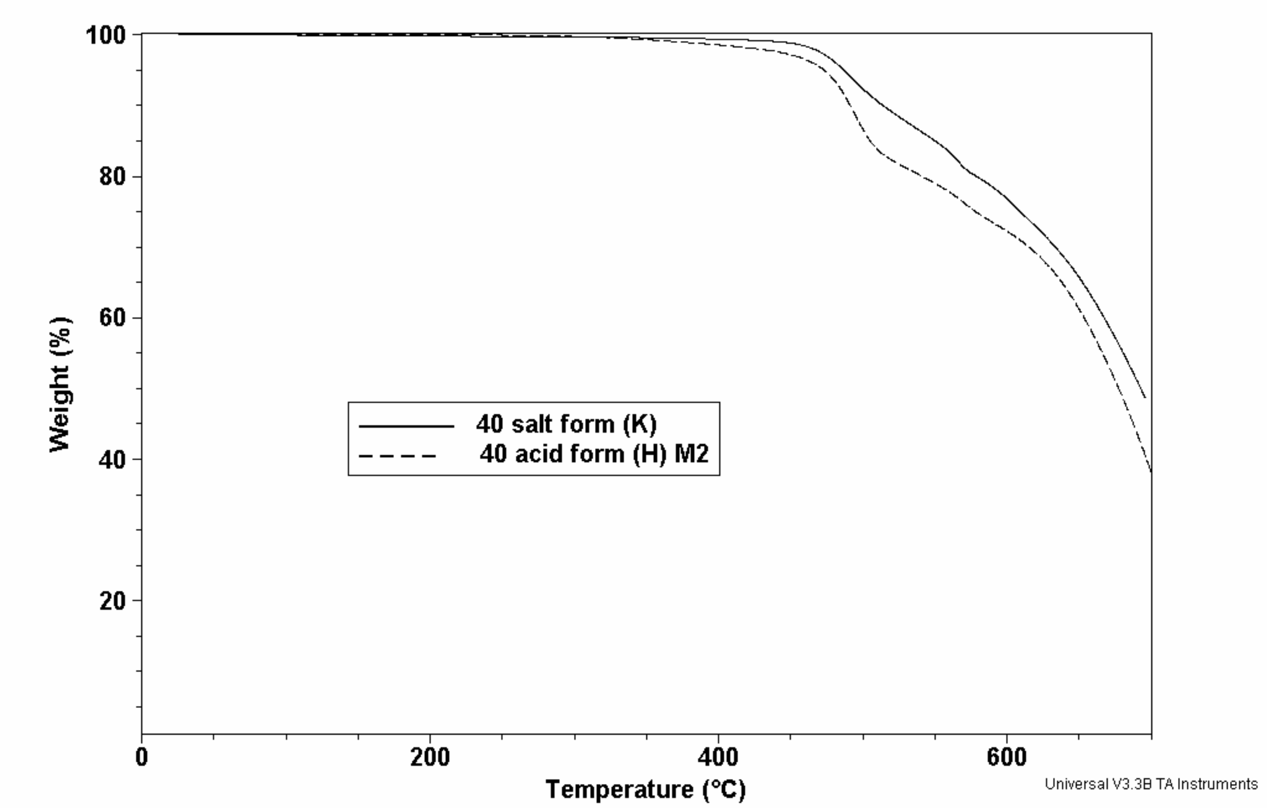


Figure 6-7. Thermogravimetric analysis of both potassium salt and sulfonic acid form 40% disulfonated copolymers

One of the fundamental membrane properties important to fuel cell performance is the water sorption, or water uptake. It is well known that PEMs must have adequate mechanical integrity when hydrated to be considered as candidates for PEM fuel cells. Recently, Kim et al. discussed the impact of the swelling and water uptake of membranes on long-term direct methanol fuel performance.[218] Since Nafion electrodes are currently used for MEA preparation, it is important that the water uptake of the membrane is similar to that of the electrodes. If the membrane swells greater than the electrodes, then the performance of the DMFC will decrease over time due to increased interfacial resistance. The water uptake measurements were performed on membranes that were soaked in 30 °C water for several days to equilibrate the samples. The water uptake values of the disulfonated benzimidazole copolymers increased with increasing degree of disulfonation, which is consistent with other poly(arylene ether) systems (Table 6-2). However, the water uptake values of these copolymers were lower than previously studied poly(arylene ether sulfone)s at comparable sulfonation levels. Therefore, the incorporation of imidazole moieties in the polymer backbone improved certain the mechanical properties of the hydrated membranes through interactions with the sulfonic acid sites.

The proton conductivities of the membranes showed quite a different trend. As the degree of disulfonation increased, the proton conductivity at 30 °C in water decreased (Table 6-2). This suggests that the proton conductivity is primarily a result of the benzimidazole moieties in the membranes. As more sulfonic acid sites are incorporated, they coordinate with the basic imidazole moieties and prevent proton conduction. As

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[218] Kim, Y.S.; McGrath, J.; Pivovar, B. The Importance of Interfaces in Membrane Optimization for DMFCs. *Abstracts of the 206th Electrochemical Society Meeting* **2004**, *2004-02*, 1471.

shown in Figure 6-8, the proton conductivity of all the membranes increased at higher temperatures under fully hydrated conditions, which is consistent with other sulfonated polymer systems.

Table 6-2. Ion-exchange capacity (IEC), water uptake, and proton conductivity data for the disulfonated copolymers

Degree of Disulfonation	IEC* (meq g^{-1})	Equivalent Weight (g meq^{-1})	Water Uptake** (%)	Conductivity** (S cm^{-1})
10	0.31	3230	8	0.011
20	0.60	1700	16	0.009
30	0.88	1140	23	0.006
40	1.15	870	29	0.004
50	1.40	710	35	0.002
Nafion 1135	0.91	1100	19	0.11

* Ion Exchange Capacity (IEC) = Degree of Disulfonation * 2 * 1000 / $Mass_{total}$
where $Mass_{total}$ = F_1(MW of nonsulfonated repeat unit) + F_2(MW of sulfonated repeat unit)
F_1 and F_2 are the respective molar ratio based on the charged diamines
**Measurements were conducted in water at 30 °C

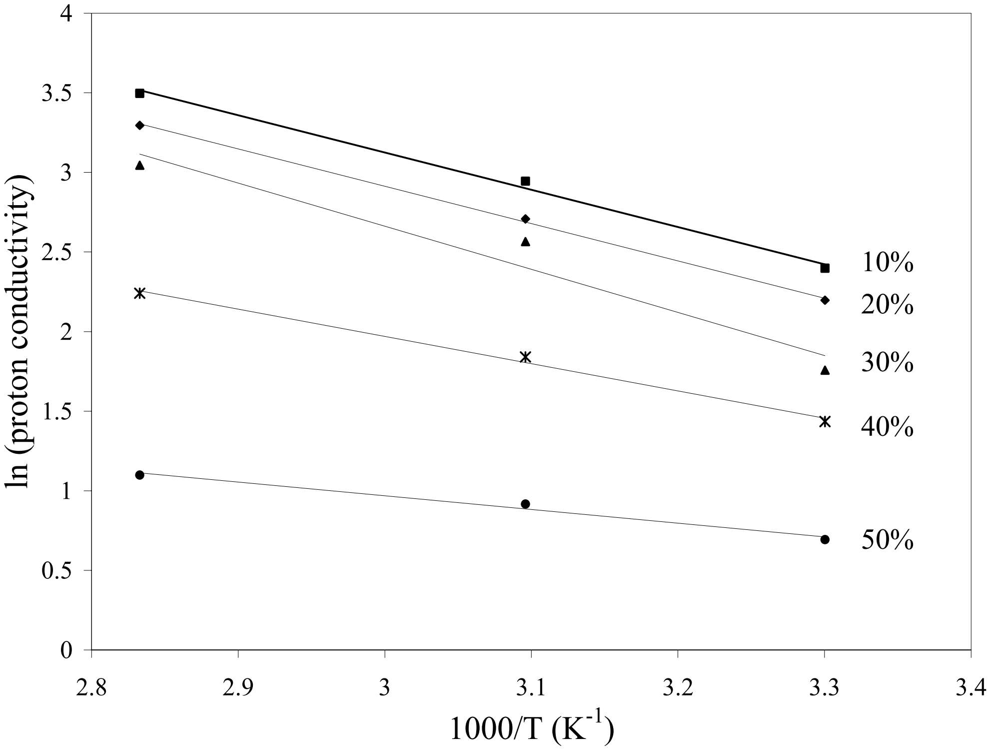

Figure 6-8. Influence of temperature on proton conductivity in liquid water

6.5. Conclusions

A systematic series of disulfonated poly(arylene ether benzimidazole) copolymers was prepared via direct copolymerization. The high molecular weight copolymers, as judged by the inherently high intrinsic viscosities, formed tough, ductile membranes when cast from DMAc. ^{1}H NMR and FT-IR confirmed the structures of the disulfonated copolymers. The water uptakes of the copolymers increased with the ion exchange capacity, similar to previously studied sulfonated polymers. However, the proton conductivity exhibited the opposite behavior, suggesting a strong interaction between the imidazole moieties and the sulfonic acid groups, which was confirmed by the improved thermal degradation of the materials.

6.6. Acknowledgments

The authors would like to thank NASA Glenn (contract #NNC04AA61A) for their support of this research effort.

CHAPTER 7

INFLUENCE OF BENZIMIDAZOLE MOIETIES ON THE SELECTED PROPERTIES OF RANDOM DISULFONATED POLY(ARYLENE ETHER) COPOLYMERS

Taken from:

Brian R. Einsla, William L. Harrison, Charles N. Tchatchoua, JamesE. McGrath. Sulfonated Poly(arylene ether benzimidazole) Copolymers for Proton Exchange Membrane Fuel Cells. Abstracts of Papers, 206th National Meeting of the Electrochemical Society, Honolulu, HI, October 3-8, 2004.

Brian R. Einsla, Melinda L. Hill, James E. McGrath. Synthesis and Characterization of Polybenzimidazole/Disulfonated Poly(arylene ether sulfone) Copolymer Blends for Proton Exchange Membrane Fuel Cells. Abstracts of Papers, Advances in Materials for Proton Exchange Membrane Fuel Cell Systems 2005, Pacific Grove, CA, February 20-23, 2005

7.1. Abstract

The influence of benzimidazole moieties on disulfonated poly(arylene ether sulfone) copolymers was studied. The addition of benzimidazole groups into random copolymers was accomplished by incorporating a benzimidazole bisphenol in the copolymerization step. Miscible (single T_g) blend membranes were prepared by addition

of separately synthesized (poly(5,5'-benzimidazole-2,2'-diyl-1,3-phenylene) (PBI) to disulfonated poly(arylene ether sulfone) copolymers (BPSH). In all cases, tough, ductile membranes were cast from N,N-dimethylacetamide solutions. The structures of the random copolymers and composition of the blend membranes were characterized via ^{1}H NMR and FT-IR. Complexation can be invoked as a mechanism for the miscibility. The thermal stability (TGA) of the membranes increased as more benzimidazole groups were incorporated, probably as a result of the complexation of the sulfonic acid groups. It was demonstrated that the proton conductivity of the membranes increased at elevated temperature and high relative humidity. In both the random copolymer and blend membranes, the introduction of benzimidazole moieties decreased the water uptake and proton conductivity of the membranes in water at 30 ^{o}C. The smallest addition of benzimidazole provided for the best selectivity, i.e. lowest drop in proton conductivity but highest decrease in water uptake.

7.2. Introduction

Proton exchange membrane fuel cell systems are environmentally attractive energy sources for a diverse array of applications including stationary power, automobiles and portable electronics.[219] The goal of many researchers in the fuel cell field is to develop novel PEMs with improved efficiency and long-term performance. Amongst many other properties, this means membranes with high proton conductivity and low water uptake. This is a difficult task because the proton conductivity is typically supplied by acidic sites that absorb water. The advantage of high proton conductivity is

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[219] Hickner, M.A.; Ghassemi, H.; Kim, Y.S.; Einsla, B.R.; McGrath, J.E. Alternative Polymer Systems for Proton Exchange Membranes (PEMs). *Chem. Rev.* **2004**, *104*, 4587-4612.

evident due to the resulting increased power density of the fuel cell. Although the need for lower water uptake may not be as obvious, high water uptake increases electroosmotic drag and can also lead to loss of mechanical strength under hydrated conditions.[220] It has also been shown that low water uptake values improve the long-term stability of membrane electrode assemblies in direct methanol fuel cells (DMFCs).[221] Furthermore, in the same discussion, it was suggested that short-term DMFC testing (1000 hours) could be used to predict the long-term stability of hydrogen-air (10,000 hours) fuel cells. Additionally, fuel cell operating conditions will include cycling, where the temperature and humidity vary greatly when the fuel cell is idle and operational. For example, a fuel cell car in cold climates will have to start at temperatures well below 0 ^{o}C, but run at higher temperatures (80 – 100 ^{o}C) under lower humidity. This temperature change will create stresses due to swelling in PEMs with high water uptakes.

The disulfonated poly(arylene ether sulfone) family of copolymers have great potential as PEMs.[222] These copolymers are prepared by direct copolymerization, which allows for increased control over the chemical composition and hence the ion exchange capacity (IEC). The result is higher acidity of the sulfonic acid sites, lower water uptake,

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[220] Wang, F.; Kim, Y.S.; Hickner, M.; Zawodzinski, T.A.; McGrath, J.E. Synthesis of Poly(arylene ether) Block Copolymers Containing Sulfonate Groups. *ACS Division of Polymeric Materials: Sci. & Eng. (PMSE)* **2001**, *85*, 517.

[221] Kim, Y.S.; McGrath, J.; Pivovar, B. The Importance of Interfaces in Membrane Optimization for DMFCs. *Abstracts of the 206th Electrochemical Society Meeting* **2004**, *2004-02*, 1471.

[222] Kim, Y.S.; Hickner, M.A.; Dong, L.; Pivovar, B.S.; McGrath, J.E. Sulfonated Poly(arylene ether sulfone) Copolymer for Proton Exchange Membranes: Composition and Morphology Effects on the Methanol Permeability. *J. Membr. Sci.* **2004**, *243*, 317-326.

and improved conductivity compared to post-sulfonated poly(arylene ether)s.[223] In particular, the wholly aromatic BPSH copolymers show similar DMFC performance to Nafion, while having lower methanol crossover.[224] A variation on the BPSH copolymers is the 6FSH series, which adds a hexafluoroisopropylidene linkage to every repeat unit of the backbone.[225] This partially fluorinated copolymer series may enhance the stability of membrane electrode assemblies (MEAs) prepared from Nafion electrodes. It has been suggested that the compatibility of the MEA could be improved due to the similar fluorinated backbones and water uptakes. Although the water uptake values of these materials are lower than post-sulfonated polymers, the directly polymerized copolymers go through a percolation threshold at higher levels of disulfonation where the water uptake increases dramatically (above 100%) and mechanical strength is lost, as illustrated in Figure 7-1.

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[223] Kim, Y.S.; Wang, F.; Hickner, M.; McCartney, S.; Hong, Y.T.; Harrison, W.; Zawodzinski, T.A.; McGrath, J.E. Effect of Acidification Treatment and Morphological Stability of Sulfonated Poly(aryleneether sulfone) Copolymer Proton-Exchange Membranes for Fuel-Cell Use Above 100 ^{o}C. *J. Polym. Sci., Part B: Polym. Phys.* **2003**, *41*, 2816-2828.

[224] Kim, Y.S.; Sumner, M.J.; Harrison, W.L.; Riffle, J.S.; McGrath, J.E.; Pivovar, B.S. Direct Methanol Fuel Cell Performance of Disulfonated Poly(arylene ether benzonitrile) Copolymers. *J. Electrochem. Soc.* **2004**, *151*, A2150-A2156.

[225] Harrison, W.L.; Wang, F.; Mecham, J.B.; Bhanu, V.A.; Hill, M.; Kim, Y.S.; McGrath, J.E. Influence of the Bisphenol Structure on the Direct Synthesis of Poly(arylene ether) Copolymers. I. *J. Polym. Sci.: Part A: Polym. Chem.* **2003**, *41*, 2264-2276.

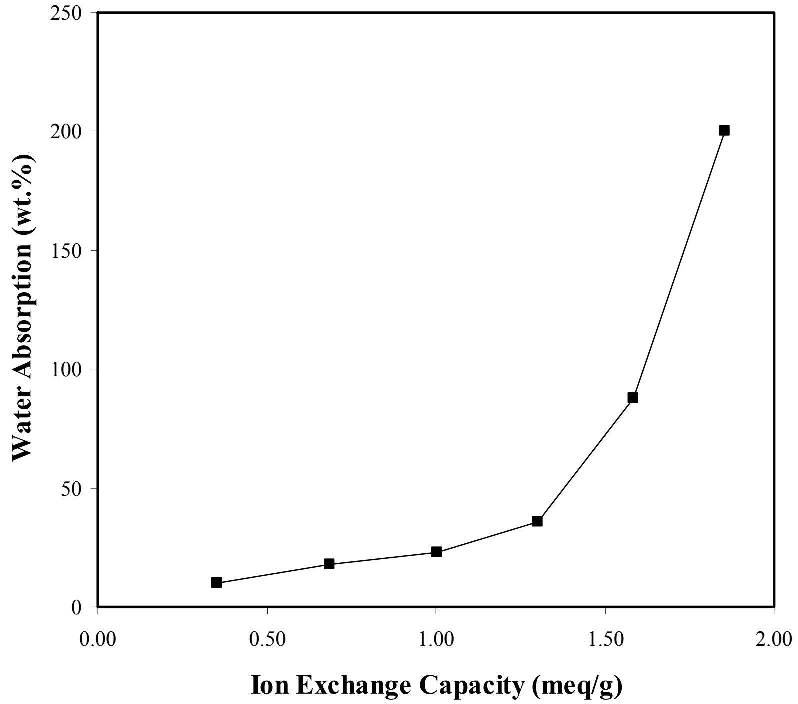

Figure 7-1. Influence of water uptake on ion exchange capacity for the 6FSH copolymers (Method 2 boiling acidification)

Disulfonated poly(arylene ether benzimidazole) copolymers possess a number of promising properties (high molecular weight, good film-formation, low water uptakes, etc.); however, their inherently low proton conductivity is a major drawback for use in PEMFCs. This effect is a result of the strong interaction between the imidazole concentrations and the sulfonic acid. In these wholly benzimidazole copolymers, the number of apparently free sulfonic acid sites was always lower than the number of benzimidazole rings. The benzimidazole groups strongly interact with the sulfonic acid, the mobility of the proton is reduced and therefore hindering conduction. The proton conductivity of the polybenzimidazole copolymers was increased via synthesis of random copolymers, where the number of sulfonic acid sites could be designed to be higher than that of the benzimidazole moieties. The strong interaction between the imidazole groups and the sulfonic acid correctly predicted that these copolymers will have lower water uptake while also promoting proton conduction, since the benzimidazole sites modestly conduct protons as well.

The swelling in post-sulfonated poly(arylene ether)s has already been reported to be reduced by adding basic groups via polymer blends.[226] High ion exchange capacities (IECs) are necessary for good proton conduction in post-sulfonated poly(arylene ether)s. These copolymers experience high water sorption values above IECs of 1.0 meq/g due to the random distribution of sulfonic acid sites along the polymer chain. The basic groups (imidazole, amine) complex with the sulfonic acid groups to reduce swelling, which would normally occur via water-sulfonic acid interactions. In particular,

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[226] Kerres, J.; Zhang, W.; Ullrich, A.; Tang, C.-M.; Hein, M.; Gogel, V.; Frey, T.; Jorissen, L. Synthesis and Characterization of Polyaryl Blend Membranes Having Different Composition, Different Covalent and/or Ionical Cross-linking Density and Their Application to DMFC. *Desalination* **2002**, *147*, 172-178.

polybenzimidazole (PBI) has been used extensively in blends with post-sulfonated Udel® poly(ether sulfone), post-sulfonated poly(ether ether ketone) (PEEK) and post-sulfonated poly(ether ketone ketone) (PEKK). Blends of post-sulfonated poly(arylene ether)s and PBI form miscible, single T_g membranes with improved thermal stability and reduced methanol crossover.[227] However, directly copolymerized poly(arylene ether sulfone)s had not been studied. Therefore, we also report the preparation and characterization of these systems and especially 6FSH-60 / PBI blends (Figures 7-10 and 7-11).

7.3. Experimental

7.3.1. Materials

4,4'-Dichlorodiphenyl sulfone (DCDPS) was kindly provided by Solvay Advanced Polymers and dried under vacuum at 60 °C before use. 4,4'-Biphenol was obtained from Honshu Chemical Ind. Co. and dried under vacuum at 60 °C. 4,4'-(Hexafluoroisopropylidene)diphenol (Bisphenol-AF) was obtained from DuPont and dried under vacuum at room temperature. The synthesis of the benzimidazole-containing bisphenol (HPBI) has been previously described by Hergenrother et al. and in the previous chapter.[228] 3,3'-Diaminobenzidine was purchased from Aldrich and dried under vacuum at room temperature. Isophthalic acid was kindly provided by Eastman and dried under vacuum at 120 °C for 24 hours before use. Potassium carbonate was purchased from Aldrich and vacuum dried at 120 °C for 24 hours before use. N,N-Dimethylacetamide (Fisher) and N-methylpyrrolidinone were distilled under reduced

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[227] Deimede, V.; Voyiatzis, G.A.; Kallitsis, J.K.; Qingfeng, L.; Bjerrum, N.J. Miscibility Behavior of Polybenzimidazole/Sulfonated Polysulfone Blends for Use in Fuel Cell Applications. *Macromolecules* **2000**, *33*, 7609 – 7617.

[228] Hergenrother, P.M.; Smith Jr., J.G.; Connell, J.W. Synthesis and Properties of Poly(arylene ether benzimidazole)s. *Polymer* **1993**, *34*, 856-865.

pressure over calcium hydride prior to use. Fuming sulfuric acid (27% SO_3), sodium chloride, sodium hydroxide, and toluene were used as received from Aldrich.

7.3.2. Monomer Synthesis: Disodium-3,3'-disulfonate-4,4'-dichlorodiphenylsulfone (S-DCDPS)

In a typical reaction, DCDPS (28.7 g, 99 mmol) was dissolved in 60 mL (390 mmol SO_3) of fuming sulfuric acid (27% SO_3) in a 100-mL, three neck flask equipped with a mechanical stirrer, condenser, and a nitrogen inlet/outlet. The solution was heated to 110 °C for 6 h to produce a homogeneous solution. The reaction was cooled to room temperature, dissolved into 400 mL of ice water, and 180 g of sodium chloride were added to produce a white precipitate of the product. The powder was filtered, redissolved in 400 mL of deionized water and neutralized to a pH of ~6-7 with aqueous 2 N sodium hydroxide. An excess of sodium chloride (~180 g) was added to salt out the sodium form of the disulfonated monomer. The crude S-DCDPS was filtered, dried and purified twice by recrystallization. The dry monomer was dissolved into 500 mL of hot methanol, filtered, and then allowed to cool to room temperature overnight. The second recrystallization was conducted in a mixture of isopropanol and water (6/1, v/v). The resulting pure product was dried at 120 °C under vacuum for at least 24 h. Yield 36.8 g (75%); ^1H NMR (400 MHz, DMSO-d_6) δ 8.33 ppm (d, 2H), 7.85 ppm (dd, 2H), 7.65 ppm (d, 2H); FT-IR (KBr) 1026 cm^{-1} (S=O, sulfonic acid, sym.), 1087 cm^{-1} (S=O sulfonic acid, asym.), 1168 cm^{-1} (S=O, sulfone); Mass Spectrum (FAB) 467 Daltons (S-DCDPS-Na^+); Elemental Analysis Calcd.: C, 27.3; H, 1.15; S, 18.2; Na, 8.72. Found: C, 27.4; H, 1.23; S, 19.3; Na, 9.36.

7.3.3. Polymer Synthesis

7.3.3.1. Synthesis of Disulfonated Poly(arylene ether sulfone benzimidazole) Copolymers

The direct synthesis of a disulfonated poly(arylene ether sulfone benzimidazole) copolymer with 40 mol % disulfonation and 10 mol % benzimidazole is discussed. The SDCDPS (3.4210 g, 7 mmol), DCDPS (2.9997 g, 10 mmol), HPBI (0.7285 g, 2 mmol), and biphenol (2.9177 g, 16 mmol) were introduced into a 250-mL, three-necked flask equipped with a mechanical stirrer, Dean-Stark trap, condenser and a nitrogen inlet/outlet. Potassium carbonate (2.77 g) and 50 mL of NMP were added to the reaction flask to afford a 20% (w/v) solid concentration. Toluene (25 mL) was added to the flask as an azeotroping agent. The Dean-Stark trap was filled with toluene and the reaction mixture was heated to 150 ^{o}C to dehydrate the system. After 4 h at 150 ^{o}C, the Dean-Stark trap was emptied and the oil bath temperature was heated to 190 ^{o}C for 24 h. The resulting viscous solution was cooled to room temperature, diluted with DMAc and precipitated into an excess of deionized water (3 L). The precipitated copolymer was collected by filtration and dried under vacuum at 80 ^{o}C for 24 h and 100 ^{o}C for 24 h.

7.3.3.2. Synthesis of 60% Disulfonated Poly(arylene ether sulfone) Copolymer Based on Bisphenol-AF (6FS-60)

First, SDCDPS (4.9120 g, 10 mmol), DCDPS (1.9145 g, 7 mmol) and Bisphenol-AF (5.6043 g, 17 mmol) were introduced into a 250-mL, three-necked flask equipped with a mechanical stirrer, a Dean-Stark trap, condenser and a nitrogen inlet/outlet. Potassium carbonate (2.77 g, 20 mmol) and 62 mL of DMAc were added to the reaction flask to afford a 20% (w/v) solid concentration. Toluene (31 mL) was added to the flask as an azeotroping agent. The Dean-Stark trap was filled with toluene and the reaction mixture was heated to 150 ^{o}C to dehydrate the system. After 4 h at 150 ^{o}C, the Dean-Stark trap was emptied and the oil bath temperature was heated to 175 ^{o}C for 48 h. The resulting viscous solution was cooled to room temperature, diluted with DMAc and precipitated into an excess of deionized water (3 L). The precipitated copolymer was collected by filtration and dried under vacuum at 80 ^{o}C for 24 h and 100 ^{o}C for 24 h.

7.3.3.3. Polybenzimidazole (PBI) Synthesis

In a typical polymerization, isophthalic acid (4.9839 g, 3 mmol), 3,3’-diaminobezidine (6.4281 g, 3 mmol) and 228 g of PPA were introduced into a 500-mL, three-necked flask equipped with a mechanical stirrer and nitrogen inlet/outlet. The mixture was stirred at 140 ^{o}C for 4 h and 200 ^{o}C for 18 h. The viscous solution was precipitated into deionized water in a high speed blender. The red, fibrous polymer was filtered, stirred in 1 L of deionized water overnight, filtered again, and washed with deionized water. The polymer was dried at 120 ^{o}C under vacuum for 48 h.

7.3.4. Membrane Preparation

Membranes were prepared by first dissolving the copolymers in DMAc at 50 ^{o}C. After filtering through a 0.45-μm Teflon membrane filter, the solution was cast directly onto a glass plate. The solvent was evaporated under infrared heat at 40 ^{o}C. The membranes were removed from the glass substrates by submersion in deionized water and then vacuum-dried at 120 ^{o}C for 24 h. The copolymer membranes were converted to their acid form by immersion in boiling 0.5 M H_2SO_4 for 2 h followed by boiling deionized water for 2h. All of the membranes were soaked in room temperature deionized water for 48 h before testing. In all cases, tough, ductile, transparent membranes were obtained.

7.3.5. Blend Membrane Preparation

A blend membrane composed of 10 wt% PBI and 90 wt% 6FS-60 is discribed. 0.09 g 6FS-60 and 0.01 g PBI were weighed directly into a 50-mL beaker. A magnetic stir-bar was added along with 30 mL of DMAc, and the mixture was stirred at 50 ^{o}C for 20 h. The transparent, reddish solution was filtered through a 0.45-μm Teflon membrane filter and directly cast onto a glass plate. The solvent was evaporated under infrared heat at 40 ^{o}C. The membranes were removed from the glass substrates by submersion in deionized water and then vacuum-dried at 120 ^{o}C for 24 h. The membranes were converted to their acid form by immersion in boiling 0.5 M H_2SO_4 for 2 h followed by boiling deionized water for 2h. All of the membranes were soaked in room temperature deionized water for 48 h before testing.

7.3.6. Characterization

^{1}H NMR spectra were recorded on a Varian Unity 400 instrument operating at 399.952 MHz, in deuterated dimethylsulfoxide (DMSO-d_6). Infrared measurements were performed on a Nicolet Impact 400 FT-IR Spectrometer from KBr pellets or solution cast films for monomers and polymer, respectively. Intrinsic viscosity (IV) measurements were conducted in either NMP or 0.05 M LiBr/NMP (where noted) at 25 ^{o}C using a Cannon Ubbelohde viscometer. Thermo-oxidative behavior of both the potassium salt-form (sulfonate) and the acid-form of the copolymers was measured on a TA Instruments TGA Q 500. Samples were dried directly in the TGA furnace at 200 °C for 2 h prior to analysis to remove water. The copolymers were evaluated from 50 °C to 800 °C in air at a heating rate of 10 °C/min.

7.4. Results and Discussion

7.4.1. Synthesis and Characterization of Random BPSH-BI Copolymers

The synthesis of wholly aromatic, biphenol-based disulfonated poly(arylene ether sulfone) copolymers (BPSH-XX) has previously been reported.[225] The ability to tailor the properties of these copolymers by controlling the ion exchange capacity in the copolymerization step is just one of many reasons why these copolymers are good candidates for proton exchange membranes. Additionally, the synthesis of disulfonated poly(arylene ether benzimidazole) copolymers, generated in an analogous method to the BPSH series but substituting a benzimidazole-bisphenol, has also been reported in the previous chapter. The proton conductivities of these materials were too low to be useful; however, the concentration of benzimidazole groups was always higher than that of sulfonic acid groups. Since the method of preparing these copolymers allows one to modify the properties easily in the copolymerization step, one could increase the proton conductivity by incorporating more sulfonic acid groups than benzimidazole moieties. Therefore, BPSH copolymers (35-45% disulfonation) were prepared with small amounts of the benzimidazole (BI) bisphenol (5-10%) added. These disulfonated BPSH-BI random copolymers were prepared via nucleophilic substitution in NMP (Figure 7-2). The copolymerizations were conducted in the presence of toluene at 150 °C for 4 hours to effectively dehydrate the system, and then the reaction temperature was increased to 190 °C until no obvious increase in viscosity was observed. During the copolymerization, the bis-phenolates that formed by reacting the bisphenols with potassium carbonate underwent a nucleophilic displacement reaction with the activated aryl halides. All of the copolymerization reactions proceeded smoothly, homogeneously, and quantitatively to afford disulfonated poly(arylene ether sulfone) copolymers with random benzimidazole concentrations.

Intrinsic viscosity values of BPSH-BI copolymers in NMP were all higher than 1.0 dL/g, demonstrating the successful polymerization of high molecular weight copolymers (Table 7-1). Additionally, the copolymers with 10% benzimidazole consistently had much higher intrinsic viscosities than the copolymers with 5% benzimidazole. This indicates that the benzimidazole moieties strongly interact with the sulfonic acid sites creating an increase in solution viscosity. This effect was further confirmed by the lower intrinsic viscosities when the measurements were conducted in 0.05 M LiBr/NMP. It is well known that charge repulsion in ionomers is responsible for the polyelectrolyte effect and a sharp rise in solution viscosity is associated with this.[229] In dilute solution, linear ionomer chains behave almost in a rod-like manner and therefore the solution viscosities increase. Using a small concentration of lithium bromide for the viscosity measurements reduced the polyelectrolyte effect associated with these copolymers.

Standardized FT-IR spectra allowed for identification of the functional groups in the copolymers. The spectra displayed the benzimidazole adsorption bands at 1716,

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[229] Katchalsky, A.; Eisenberg, H. Molecular Weight of Polyacrylic and Polymethacrylic Acid. *J. Polym. Sci.* **1951**, *6*, 145-154.

1678, and 1349 cm^{-1}, as well as those associated with the sulfonic acid groups (Figure 7-3). The symmetric and asymmetric stretches of the sulfonate groups appeared at 1030 and 1097 cm^{-1}, respectively. The intensities of the peaks at 1030 and 1097 cm^{-1} increased with the degree of disulfonation. The molecular structure of the BPSH-BI copolymers was also confirmed by ^1H NMR (Figure 7-4). The introduction of the sulfonate groups was also confirmed by the proton resonances at 7.00, 7.85, and 8.30 ppm, as previously reported.[230] The quantitative degree of disulfonation was calculated by integration of peaks in the sulfonated and nonsulfonated regions and using the formula shown in Figure 7-5. The calculated values for the degree of disulfonation were converted to ion exchange capacities. These experimental values compare well with the calculated values established by the feed ratios of the monomers in the copolymerization (Table 7-2).

Tough, ductile, transparent membranes were prepared by dissolving the copolymers in their sulfonate-salt forms in DMAc followed by casting onto clean, glass substrates. The solvent was evaporated under IR lamps and the membranes were lifted from the glass plates by immersion in deionized water. The acid-form membranes were prepared by boiling in dilute sulfuric acid and the conversion was confirmed by the absence of potassium in the x-ray photoelectron spectrum (Figure 7-6).

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[230] Wang, F.; Hickner, M.; Kim, Y.S.; Zawodzinski, T.A.; McGrath, J.E. Direct Polymerization of Sulfonated Poly(arylene ether sulfone) Random (Statistical) Copolymers: Candidates for New Proton Exchange Membranes. *J. Membr. Sci.* **2002**, *197*, 231-242.

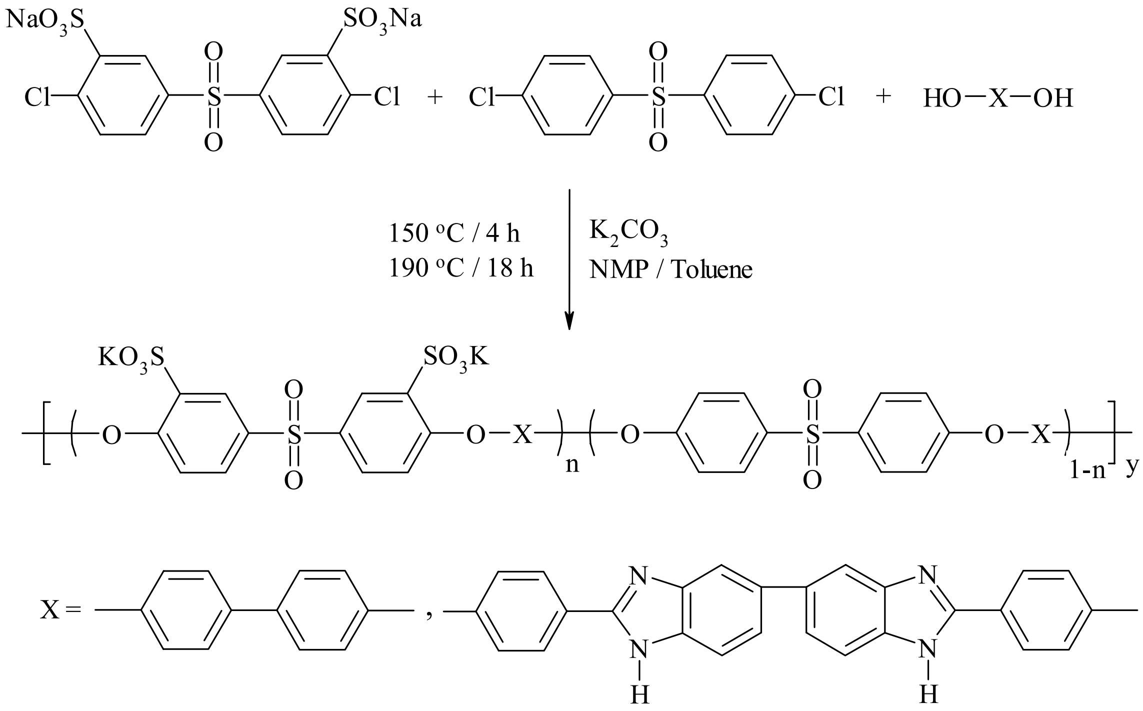


Figure 7-2. Synthesis of BPSH-BI random copolymers

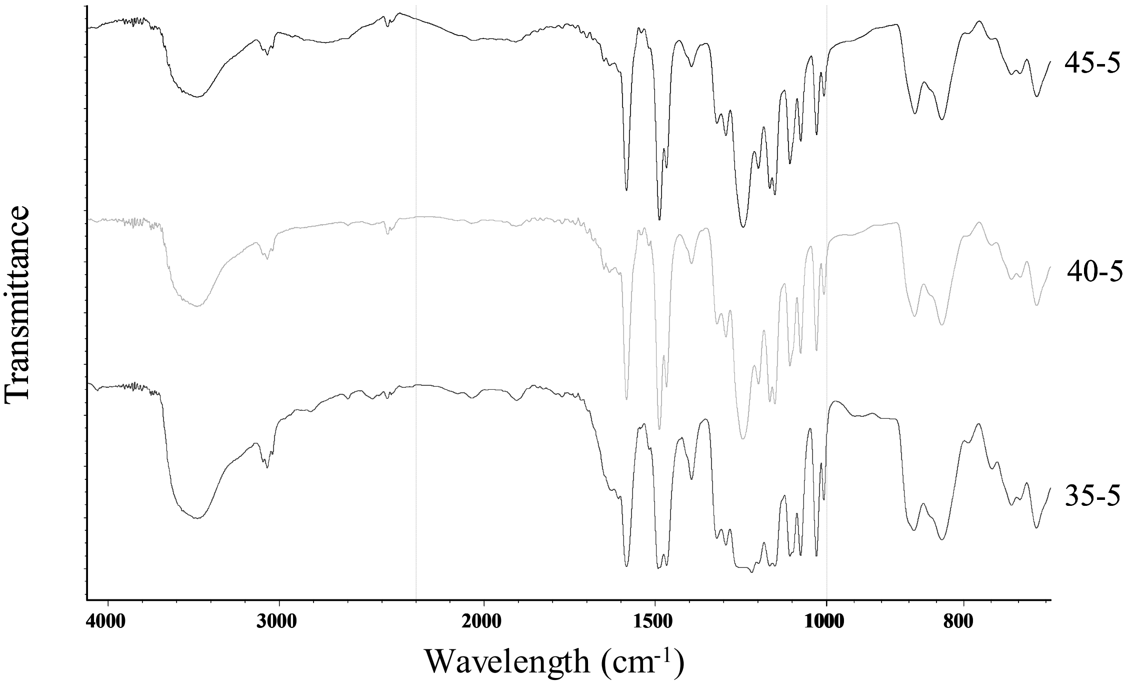


Figure 7-3. FT-IR of BPSH-BI copolymers with 5% benzimidazole

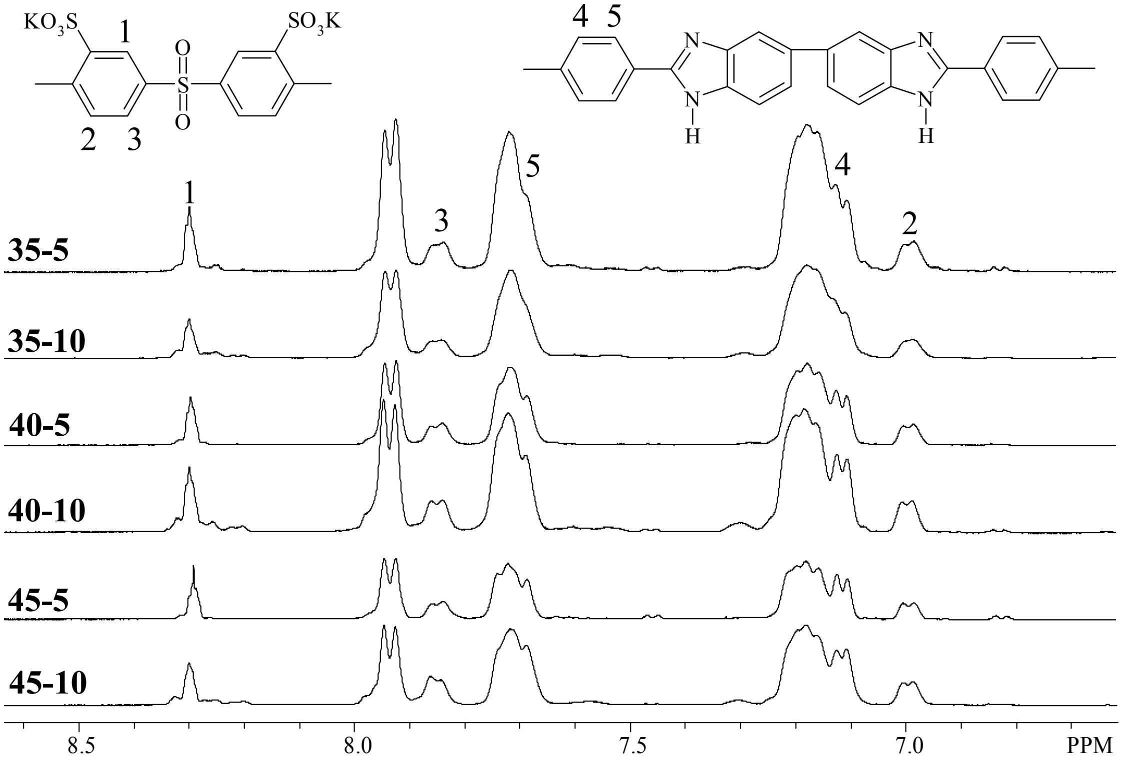
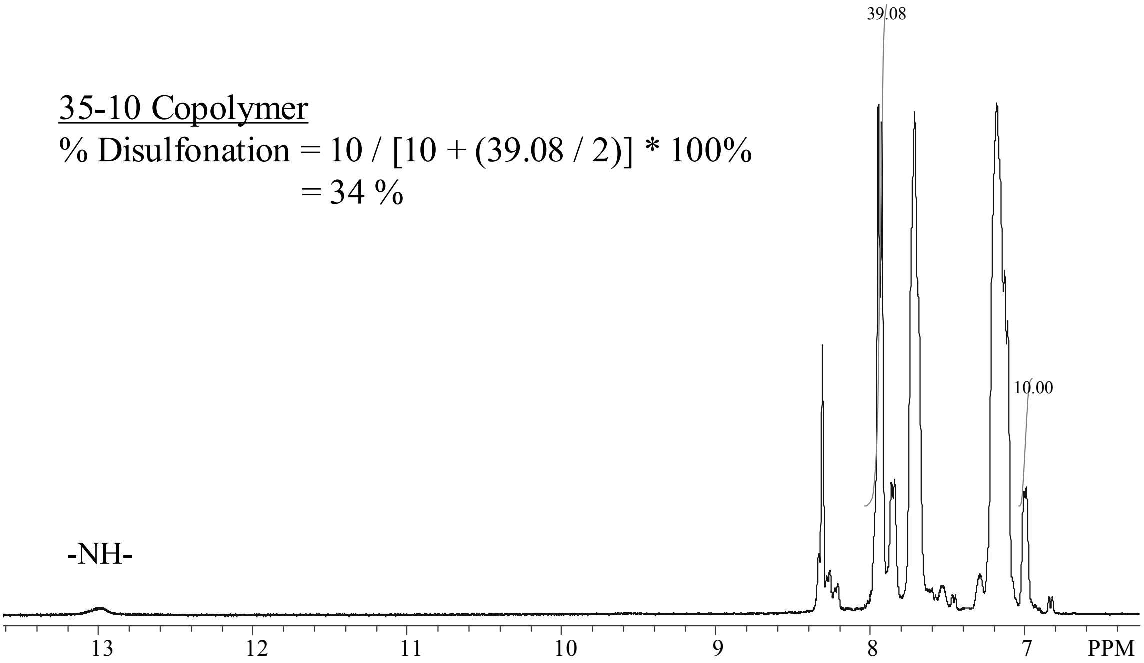


Figure 7-4. ^{1}H NMR and structural assignment of BPSH-BI copolymers (DMSO-d_6)



35-10 Copolymer

% Disulfonation = 10 / [10 + (39.08 / 2)] * 100%
= 34 %

Figure 7-5. Determination of copolymer composition via ^{1}H NMR

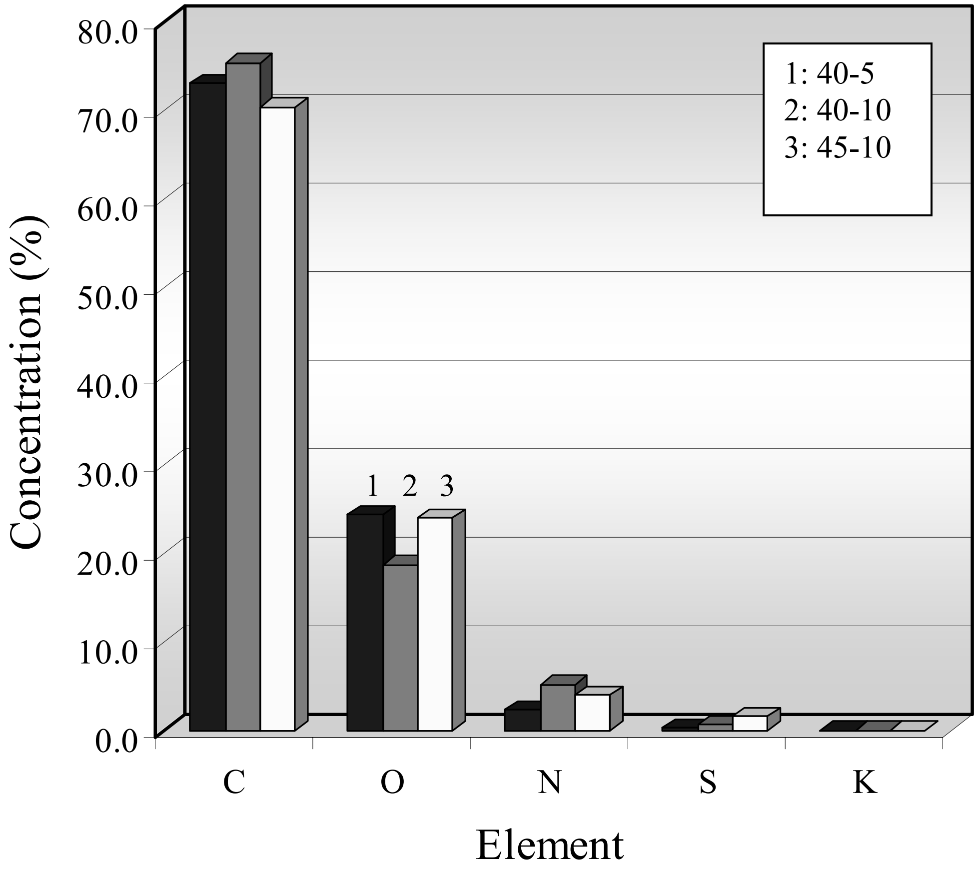


Figure 7-6. XPS of BPSH-BI Copolymers: 1: 40-5, 2: 40-10, and 3: 45-10

7.4.2. Water Uptake of BPSH-BI Copolymers

The water uptake values of the membranes were measured at 30 °C and were a function of the degree of disulfonation and the amount of benzimidazole incorporated (Table 7-3 and Figure 7-7). Not surprisingly, the water uptake increased with sulfonation and decreased with the addition of benzimidazole groups. The interaction of the sulfonic acid groups and the benzimidazole moieties reduced the ability of the sulfonate groups to absorb water. The change in water uptake (shown as a percentage) was determined to establish the effect the benzimidazole concentrations. For the 35 and 40% copolymers, the addition of benzimidazole groups influenced the water sorption by the same amount. As 5 mole % of the benzimidazole monomer was added, the water uptakes dropped by 16%. However, upon addition of 5% more benzimidazole monomer, the water uptakes decreased by just an additional 12%. The influence of the benzimidazole moieties on the water uptake of the 45% disulfonated copolymers was slightly larger. This effect can be explained by taking into account the morphology of the membranes. The water uptake and its correlation to the morphology of the BPSH copolymers has been well studied.[231] When BPSH membranes were acidified under boiling conditions, the water uptake increased monotonically to 40% disulfonation (Figure 7-1). At higher levels of disulfonation, the water uptake increased more rapidly. The change in slope of the plot of the water uptake versus degree of disulfonation was attributed to a percolation threshold. At less than or equal to 40% disulfonation, the hydrophobic domains were the continuous phase; at higher levels of disulfonation, the hydrophilic domains were continuous. By adding the benzimidazole comonomer to the 45% disulfonated

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[231] Kim, Y.S.; Dong, L.; Hickner, M.A.; Pivovar, B.S.; McGrath, J.E. Processing Induced Morphological Development in Hydrated Sulfonated Poly(arylene ether sulfone) Copolymer Membranes. *Polymer* **2003**, *44*, 5729-5736.

copolymer, the water uptake resembled that of membranes below the percolation threshold.

Table 7-1. Nomenclature and characterization of BPS-BI copolymers

BPS-BI Copolymer Designation	Monomer Concentration (mol)				Yield (%)	Intrinsic Viscosity (dL/g)*	
	SDCDPS	DCDPS	HPBI	Biphenol		NMP	0.05 M LiBr / NMP
35-5	0.35	0.65	0.05	0.95	98	1.5	1.1
35-10	0.35	0.65	0.10	0.90	97	2.4	1.3
40-5	0.40	0.60	0.05	0.95	98	1.3	1.0
40-10	0.40	0.60	0.10	0.90	99	2.5	1.2
45-5	0.45	0.55	0.05	0.95	99	1.8	1.1
45-10	0.45	0.55	0.10	0.90	96	2.4	1.6

* Measurements made at 25 ^{o}C

Table 7-2. Ion Exchange Capacity (IEC) of BPSH-BI membranes

Copolymer	Equivalent Weight (g meq^{-1})	Calculated IEC (meq g^{-1})	Experimental IEC* (meq g^{-1})	mol -SO_3H / mol BI
35-5	775	1.29	1.18	7.0
35-10	943	1.06	1.00	3.5
40-5	676	1.48	1.50	8.0
40-10	794	1.26	1.25	4.0
45-5	599	1.67	1.52	9.0
45-10	694	1.44	1.45	4.5

* Determined by ^{1}H NMR

Table 7-3. Effect of Benzimidazole (BI) Concentrations on Water Uptake at 30 °C

Degree of Disulfonation (%)	**Water Uptake (%)**			**Change in Water Uptake (%)**		
	0% BI	5% BI	10% BI	Δ_{0-5}	Δ_{5-10}	Δ_{0-10}
35	38	32	28	16	12	26
40	58	49	43	15	12	26
45	100	65	55	35	15	45

Δ_{1-2} = 100 * [Water Uptake of 1 - Water Uptake of 2] / Water Uptake of 1

Table 7-4. Effect of Benzimidazole (BI) Concentrations on Proton Conductivity at 30 °C

Degree of Disulfonation (%)	Proton Conductivity, σ (S/cm)			Change in Conductivity (%)		
	Control	5% BI	10% BI	Δ_{0-5}	Δ_{5-10}	Δ_{0-10}
35	0.08	0.014	0.007	82	50	91
40	0.10	0.020	0.011	80	45	89
45	0.12	0.036	0.015	70	58	88

$\Delta_{1\text{-}2} = 100 * [\sigma_1 - \sigma_2] / \sigma_1$

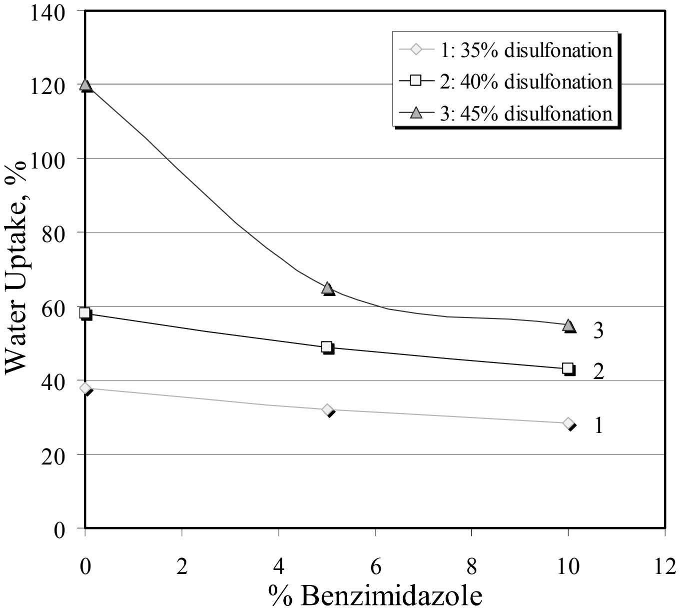

Figure 7-7. Influence of benzimidazole moieties on the water uptake of BPSH-BI copolymers

7.4.3. Proton Conductivity of BPSH-BI Copolymers

The proton conductivities at 30 °C showed similar trends to water uptake (Table 7-4). The addition of the first 5 mol% of benzimidazole monomer had a larger effect on the proton conductivity than did further addition. Unlike the percolation threshold in the water uptake values, the proton conductivity plot is linear as a function of degree of disulfonation. Therefore, all of the samples surprisingly show similar changes in proton conductivity as benzimidazole groups are added, independent of degree of disulfonation. For example, going from 0% to 10% benzimidazole consistently resulted in a 90% decrease in proton conductivity for all samples. Similar to previous results, the proton conductivities increased at higher temperatures under fully hydrated conditions (Figure 7-8).

Under typical hydrogen-air fuel cell conditions, the membrane will be operated at high temperature (80-120 °C) and will not be fully humidified (20-50% RH). This simplifies the water management system, increases reaction kinetics and reduces carbon monoxide poisoning of the precious catalyst.[219] The high temperature also promotes proton conduction, while low relative humidity inhibits conduction. Proton transport in sulfonic acid-based materials is driven by the presence of water; therefore it is necessary to study the effect of humidity on proton conductivity in different membranes. It is the goal of most automobile companies to operate at 100-120 °C and below 50% relative humidity. Unfortunately, the expensive platinum catalysts currently used in the electrodes are not stable above 80 °C.[232] Therefore, the proton conductivities of two BPSH-BI membranes, 40-5 and 45-10, were tested at 80 °C and low relative humidity

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[232] Mathias, M.; Gasteiger, H.; Makharia, R.; Kocha, S.; Fuller, T.; Xie, Tao, Pisco, J. Can Available Membranes and Catalysts Meet Automotive Polymer Electrolyte Fuel Cell Requirements? *ACS Div. Fuel Chem.* **2004**, *49,* 471-474.

(Figure 7-9). The proton conductivities of the membranes were similar under all conditions due to their similar ion exchange capacities, yet the conductivities were still lower than Nafion®.

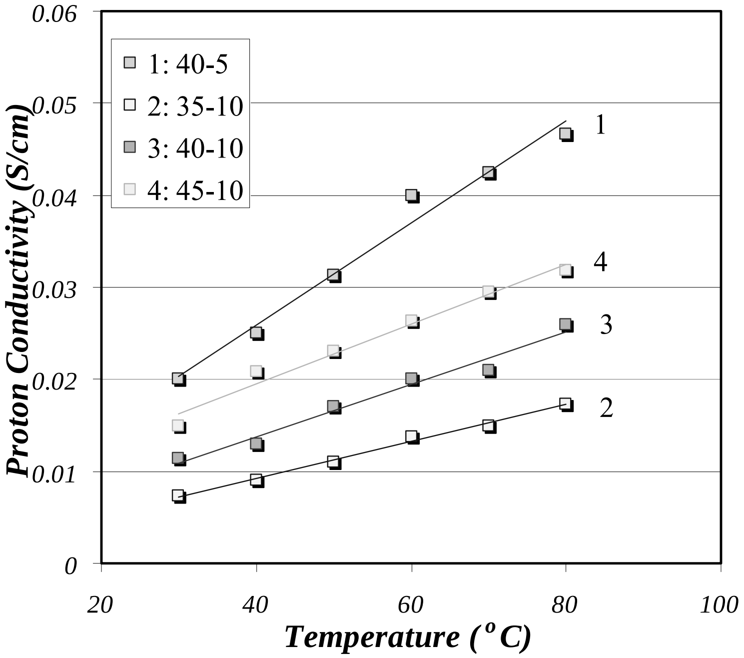

Figure 7-8. Effect of temperature on proton conductivity of BPSH-BI membranes in liquid water

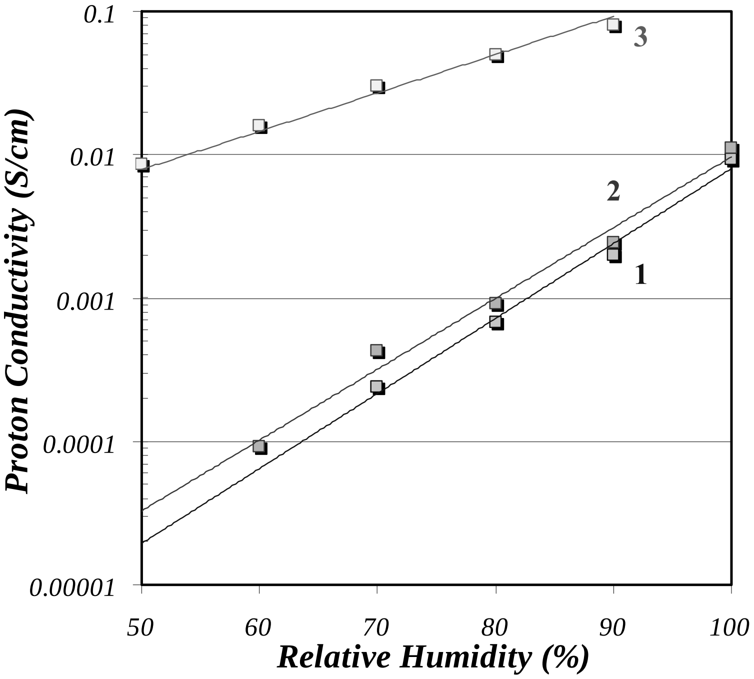

Figure 7-9. Effect of relative humidity on proton conductivity at 80 °C of (1) 40-5, (2) 45-10, and (3) Nafion 1135

7.4.4. Synthesis and Characterization of 6FSH-60

In previous work, the incorporation of PBI into post-sulfonated poly(arylene ether)s lowered the proton conductivity as well as the water sorption, so it was necessary to use a highly sulfonated copolymer.[233] The synthesis of the partially fluorinated disulfonated poly(arylene ether sulfone) copolymers (6FSH) has been reported.[225] At high degrees of disulfonation (> 40%), it was difficult to synthesize high molecular weight copolymers using disodium-3,3'-disulfonate-4,4'-dichlorodiphenylsulfone (S-DCDPS). Another procedure was introduced using the highly activated but more costly difluoro monomers, S-DFDPS and DFDPS, to produce high molecular weight copolymers. Herein, an alternative method to obtain high molecular weight copolymers from S-DCDPS at high ion exchange capacities (IECs) is presented. The conversion of DCDPS to S-DCDPS by the reported conditions was quantitative with no side-products.[234] The only impurity introduced was sodium chloride upon precipitation and isolation. A method was described to calculate the amount of salt present in S-DCDPS and use this monomer to produce high molecular weight copolymers. Another procedure is described herein where the S-DCDPS was recrystallized in methanol to remove the salt impurity. The crude S-DCDPS was dissolved in hot methanol, filtered to remove sodium chloride, and allowed to cool to room temperature, which crystallized pure S-DCDPS. After filtration, excess methanol could also be removed by vacuum distillation to obtain pure S-DCDPS. High molecular weight 6FS-60 (IEC = 1.86 meq/g) was synthesized

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[233] Jorissen, L.; Gogel, V.; Kerres, J.; Garche, J. New Membranes for Direct Methanol Fuel Cells. *J. Power Sources* **2002**, *105*, 267-273.

[234] Sankir, M. Bhanu, V.A.; Ghassemi, H.; Wiles, K.B.; Hill, M.L.; Harrison, W.; Sumner, M.; Glass, T.E.; Riffle, J.S.; McGrath, J.E. Systematic Study of the Synthesis and Characterization of 3,3'-Sulfonylbis(6-chlorobenzenesulfonic acid) Disodium Salt Monomer for Proton Conducting Polymeric Membranes in Fuel Cell Applications. *ACS Div. Polym. Chem., Polym. Preprs.* **2003**, *44,* 1079-1080.

using this purified monomer (Figure 7-10). The intrinsic viscosity (IV) of this copolymer was measured in NMP and 0.05 M LiBr at 25 ºC. The IV of 6FS-60 in NMP was found to 2.7 dL/g, which is close to the value previously reported for the copolymerization using the highly activated S-DFDPS (2.5 dL/g). The dilute solution viscosity measurements were also conducted in 0.05 M LiBr/NMP to eliminate the polyelectrolyte effect in these sulfonated copolymers. The IV in LiBr/NMP was 0.91 dL/g. The 6FS-60 was characterized by ^{1}H NMR and FTIR to confirm the structure of the copolymer (Figures 7-12 and 7-13).

7.4.5. Synthesis of Poly(5,5'-benzimidazole-2,2'-diyl-1,3-phenylene) (PBI)

Polybenzimidazole, PBI (poly(5,5'-benzimidazole-2,2'-diyl-1,3-phenylene), is a high-temperature polymer that is known for its excellent thermal stability, flame resistance, mechanical properties, and acid and base resistance. PBI is made commercially by Celanese via melt polymerization of 3,3'-diaminobenzidine (DAB) and diphenyl isophthalate at high temperature (300 °C). An alternative route was introduced by Hein et al. in 1957 using DAB and the less expensive isophthalic acid in polyphosphoric acid (PPA).[235] Recently, Beneciweicz et al. have discussed the influence of reaction conditions (temperature, monomer concentration, and reaction time) on the molecular weight of PBI.[236] Higher molecular weights were achieved using the PPA process (>2 dL/g) compared to the conventional melt polymerization (0.6-0.8 dL/g).

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[235] Hein, D. W.; Alheim, R. J.; Leavitt, J. J. The Use of Polyphosphoric Acid in the Synthesis of 2-aryl- and 2-alkyl-Substituted Benzimidazoles, Benzoxazoles, and Benzothiazoles. *J. Am. Chem. Soc.* **1957**, *79*, 427-429.

[236] Benicewicz, B. Advances in Polybenzimidazole Synthesis and Applications to Fuel Cells. *Polycondensation 2004*, September 26-29, 2004, Abstract 30; Benicewicz, B. *Science* **2005**, *in press.*

Herein, the polymerization of PBI was conducted in PPA at 5 wt. % solids concentration (Figure 7-11). The temperature of the reaction was first increased to 140 °C to dissolve the monomers and prevent the isophthalic acid from subliming out of the reaction. Once the reaction became homogeneous, the temperature was increased to 200 °C to complete the polymerization. The viscous solution was precipitated in deionized water and neutralized with base. The neutralization step is necessary to dissolve PBI in organic solvents such as DMAc. The precipitation process turns PPA to phosphoric acid, which protonates the imidazole ring, making PBI insoluble in DMAc.

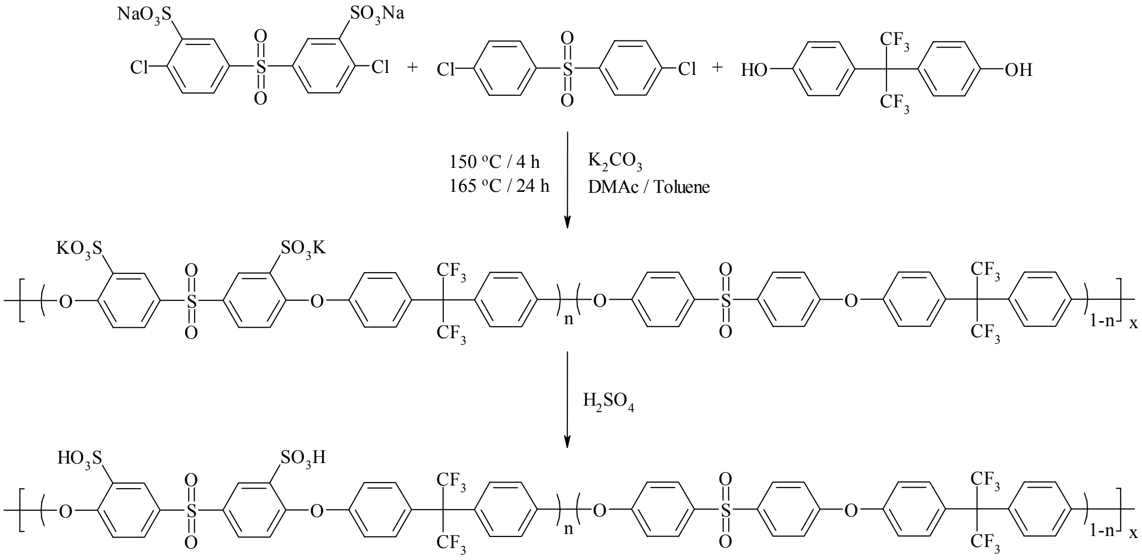

Figure 7-10. Direct synthesis of 6FSH-XX copolymers

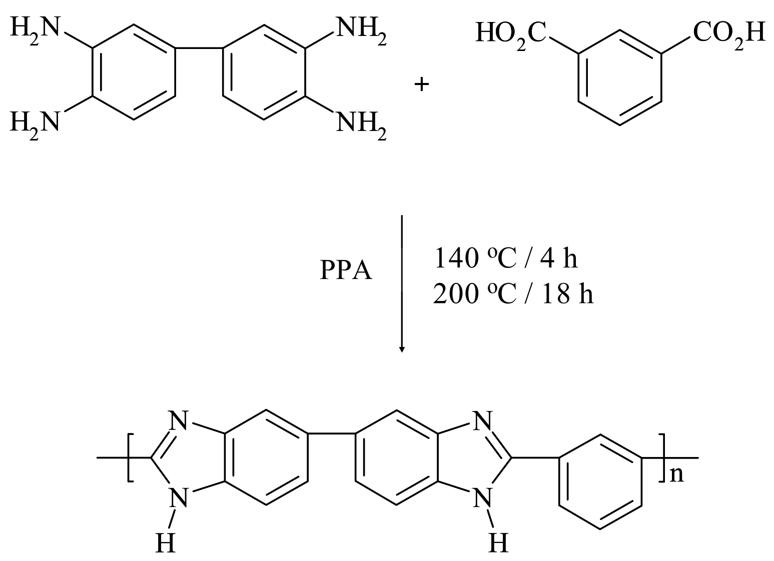

Figure 7-11. Synthesis of polybenzimidazole (PBI) in polyphosphoric acid (PPA)

7.4.6. Composition and Properties of 6FSH-60/PBI Blend Membranes

Copolymer-homopolymer blend membranes composed of 5, 10, 20 and 30 weight percent PBI in 6FS-60, were prepared by dissolving the polymers in DMAc and solution casting. The acid-form membranes were generated by boiling the membranes in dilute sulfuric acid. Blends of PBI and polysulfone are immiscible.[237] On the other hand, the incorporation of ionic groups such as sulfonate groups resulted in miscible blends, at concentrations of PBI up to 30%. Blends of 6FSH-60 with 5, 10, and 20% PBI resulted in tough, ductile, transparent membranes, whereas the 30% PBI membranes were opaque. A possible reason for this incompatibility may be the ratio of sulfonic acid groups to imidazole moieties. At 5, 10 and 20% PBI, the number of sulfonic acid groups is greater than imidazole. However, the 30% PBI blend membrane has more imidazole concentrations than sulfonic acid sites. The incorporation of PBI in the blend membranes was confirmed by FT-IR and ^{1}H NMR. PBI shows a strong absorbance at 1440 cm^{-1} in the FT-IR spectrum which is not overshadowed by stronger signals of 6FS-60, so this peak was selected to monitor the incorporation of PBI in the blend membranes (Figure 7-12). In the ^{1}H NMR, the incorporation of PBI into 6FS-60 was demonstrated by the additional resonances at 9.15 ppm corresponding to the protons on the nitrogen atoms, and the peaks at 7.60 and 7.75 ppm due to the protons on the aromatic rings of PBI (Figure 7-13).

The thermal stability of 6FSH-60, PBI and the blend membranes were determined by thermogravimetric analysis in air. A two-step degradation profile was observed for 6FSH-60 and the blend membranes (Figure 7-14). The initial weight loss of the 6FSH-60

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[237] Deimede, V.; Voyiatzis, G.A.; Kallitsis, J.K.; Qingfeng, L.; Bjerrum, N.J. Miscibility Behavior of Polybenzimidazole/Sulfonated Polysulfone Blends for Use in Fuel Cell Applications. *Macromolecules* **2000**, *33*, 7609 – 7617.

membrane around 300 ^{o}C was assigned to desulfonation while the weight loss at 450 ^{o}C was attributed to the main chain polymer degradation. The 5% weight loss increased from 361 ^{o}C (6FSH-60) to 471 ^{o}C (30% PBI) as more PBI was incorporated.

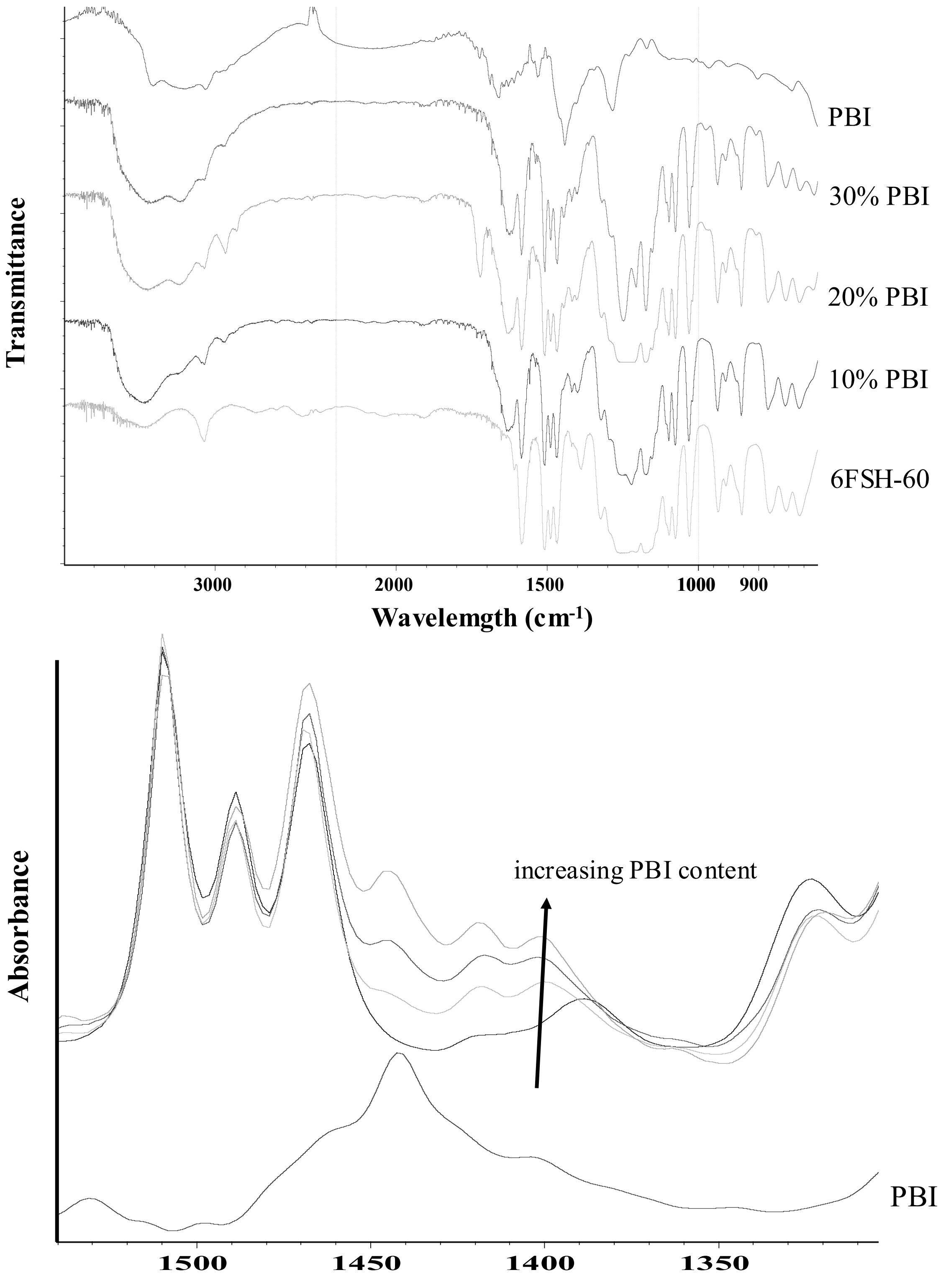

Figure 7-12. FTIR spectra of 6FSH-60, PBI and Their Copolymer Blends

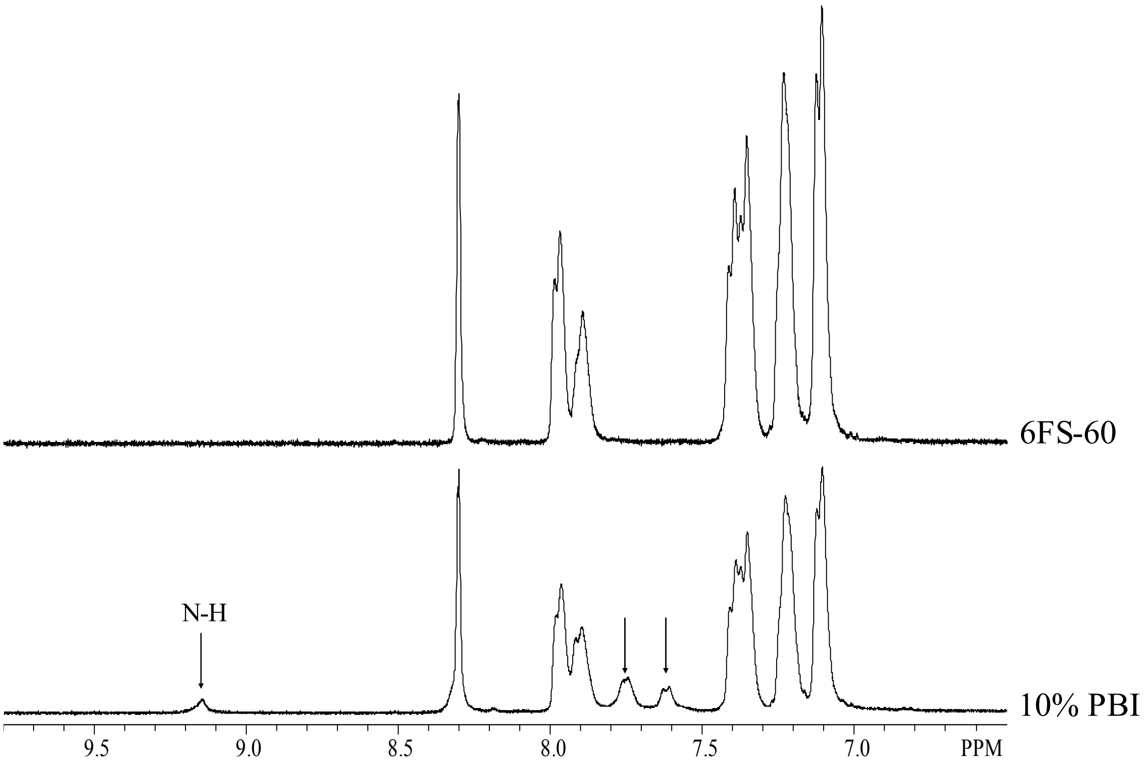

Figure 7-13. ^{1}H NMR of 6FS-60 (top) and a 6FS-60/10%PBI blend (bottom) (DMSO-d_6)

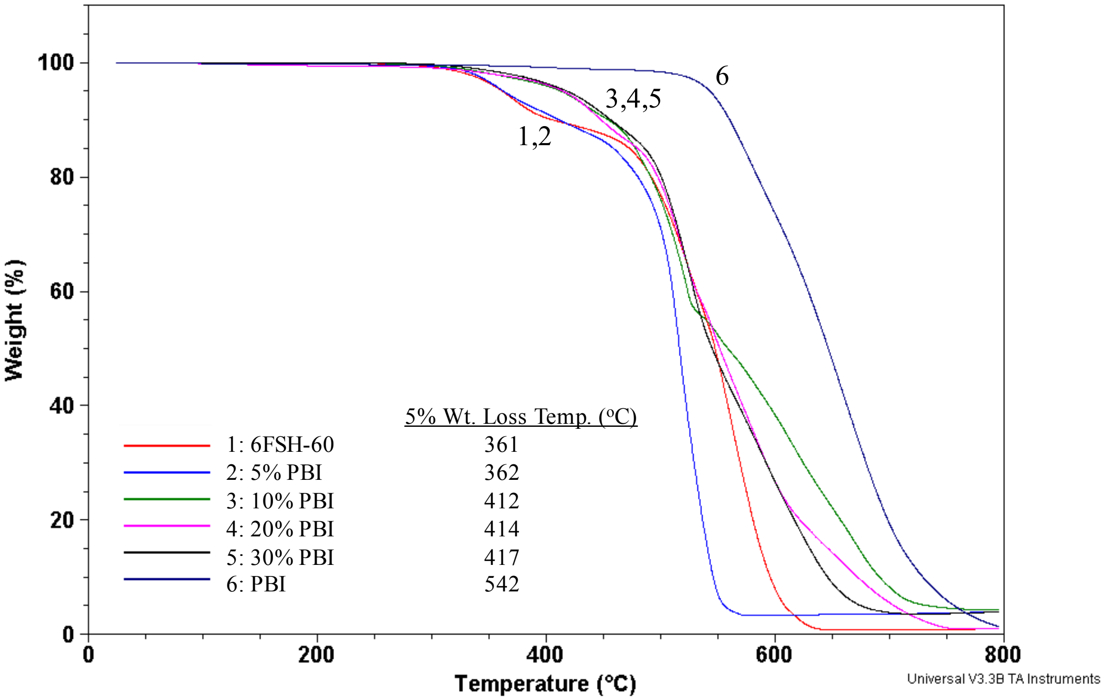

Figure 7-14. Thermogravimetric analysis of 6FSH-60, PBI and their copolymer blends

7.4.7. Water Uptake and Proton Conductivity of 6FSH-60/PBI Blends

It has been shown that blend membranes composed of post-sulfonated polysulfone and PBI have lower water sorption, proton conductivity and methanol permeability compared to the sulfonated polysulfone alone.[238] Similar to the random copolymers discussed above, the water uptake and proton conductivity in water at 30 °C decreased as more benzimidazole moieties were incorporated (Table 7-5). When only 5% PBI was added, the water uptake decreased to about one-third of the water uptake of 6FSH-60, but the proton conductivity decreased by only about one-half. The effect of PBI on water uptake was less pronounced as the amount of PBI increased to 20%, while the drop in proton conductivity was more prominent. At 30% PBI, the water uptake increased to 30.5%, probably due to the immiscible blend at that composition. Additionally, the proton conductivity values of the blend membranes in water increased with temperature and relative humidity, similar to the random copolymers discussed above (Figures 7-15 and 7-16). Particularly interesting are the 6FSH-60 and 6FSH-60/5% PBI membranes at 80 °C and low relative humidity. Both membranes showed proton conductivity values close to Nafion® 1135, suggesting that these would be good candidates for H_2/air PEMFCs.

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[238] Manea, C.; Mulder, M. New Polymeric Electrolyte Membranes Based on Proton Donor-Proton Acceptor Properties for Direct Methanol Fuel Cells. *Desalination* **2002**, *147*, 179 – 182.

Table 7-5. Properties of 6FSH-60, Copolymer Blends and Nafion

Sample	mol -SO_3H / mol benzimidazole	Water Uptake* (%)	Proton Conductivity* (S/cm)
6FSH-60	-	200.0	0.22
5% PBI	5.4	60.1	0.094
10 % PBI	2.6	26.6	0.013
20% PBI	1.1	20.1	0.0013
30% PBI	0.7	30.5	0.00091
Nafion 1135	-	19.0	0.11

*** Measurements conducted in liquid water at 30 ^{o}C**

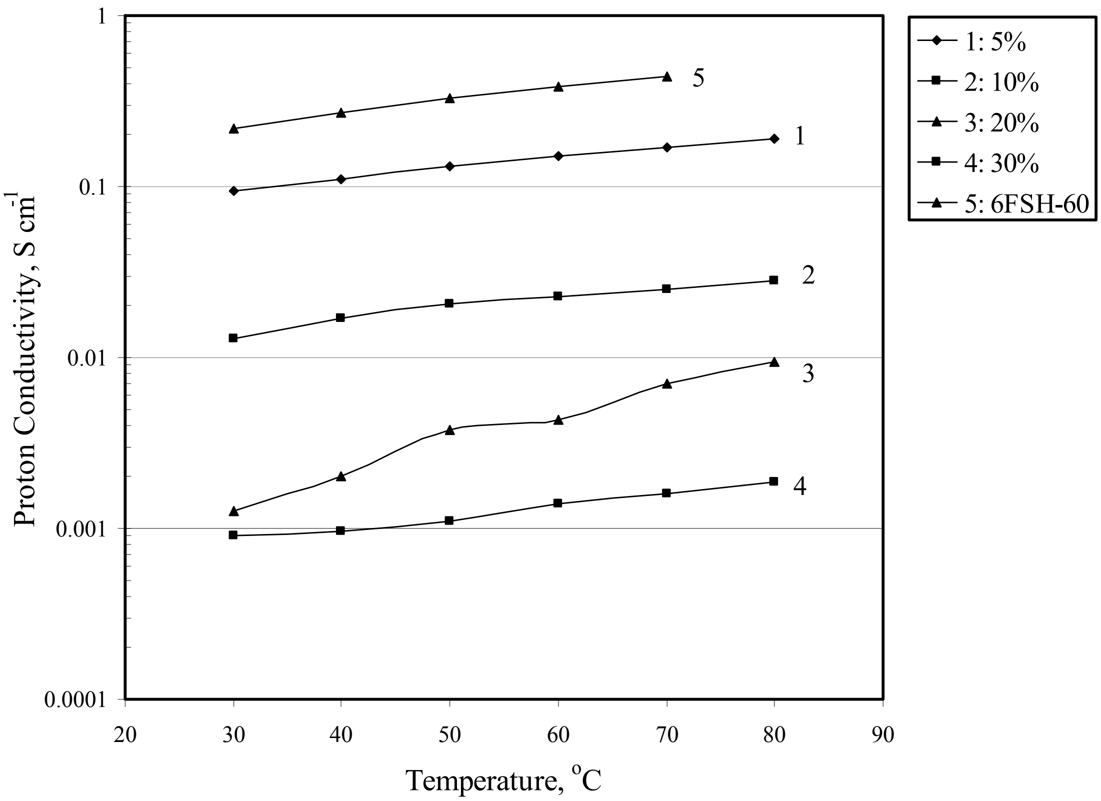

Figure 7-15. Effect of temperature on proton conductivity of 6FSH-60 and its blends with PBI

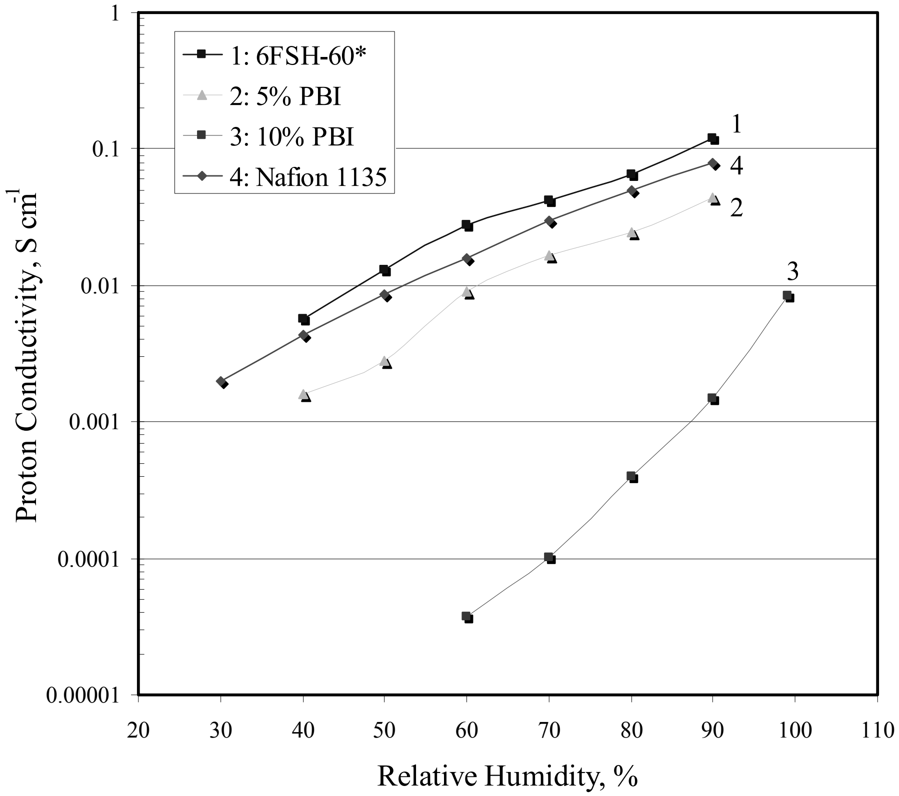

Figure 7-16. Effect of relative humidity on proton conductivity at 80 °C of (1) 6FSH-60, (2) 6FSH-60/5% PBI, (3) 6FSH-60/10% PBI and (4) Nafion 1135.

Conclusions

Incorporating small amounts of benzimidazole into random copolymers had an enormous affect on proton conductivity and water sorption. It may be suggested that going to higher ion exchange capacities in the random BPSH-BI copolymers should increase the proton conductivities of these membranes. However, the 45% disulfonated copolymer with benzimidazole displayed relatively high water uptake values. Therefore, going to higher IECs would be advantageous for proton conduction, yet the water uptake may be too high to be useful. On the other hand, the blend membranes showed fairly good proton conductivities at low levels of PBI incorporation. At >10% PBI, the proton conductivity of the membranes was too low to be useful for PEMs. It is clear that the blend membranes were better suited for fuel cell applications; however, further research is needed to optimize this system (ion exchange capacity of 6FSH and concentration of PBI). Although the low proton conductivities may limit the use of these copolymers for hydrogen/air fuel cells, they may be applicable to direct methanol fuel cells (DMFCs). Other researchers have shown that the incorporation of benzimidazole groups lowers the methanol permeability of the membrane.[238] While proton conduction is necessary, a major factor in the performance of a DMFC is the methanol permeability of the membrane. The lower water sorption of the blend membranes may suggest that the methanol permeability of these membranes would decrease as well.

Acknowledgements

The authors would like to than Frank Cromer for XPS analysis. The authors would also like to thank NASA Glenn (contract #NNC04AA61A) for their support of this research effort.

CHAPTER 8

SYNTHESIS AND CHARACTERIZATION OF HYDROXYL-FUNCTIONALIZED POLY(ARYLENE ETHER SULFONE) COPOLYMERS AND CONVERSION TO PROTON-CONDUCTING MEMBRANES FOR FUEL CELLS

Taken from:
Brian R. Einsla, James E. McGrath. Synthesis and Characterization of Hydroxy-Functionalized Poly(arylene ether sulfone)s and Conversion to Proton Conducting Membranes for Fuel Cells. *American Chemical Society Division of Fuel Chemistry* **2004**, *49*, 616-618.

8.1. Abstract

Sulfonated poly(arylene ether sulfone) copolymers with pendent sulfonic acid groups were synthesized by the direct copolymerization of methoxy-containing poly(arylene ether sulfone)s, then converting the methoxy groups to the reactive hydroxyl form, and finally functionalizing the hydroxyl form with proton-conducting sites through nucleophilic substitution. The functionalization reactions to achieve proton-conducting copolymers were conducted at low temperature (80°C) to minimize the ether-ether interchange reactions that occur in poly(arylene ether)s in the presence of base. The copolymers were characterized by intrinsic viscosity (IV), ^{1}H nuclear magnetic resonance

(NMR), infrared spectroscopy, thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC) to verify their structures. The IV and glass transition temperature (T_g) both increased after the conversion of the methoxy groups to hydroxyl due to an increase in intermolecular interactions. However, there was no change in the TGA data. Once the sulfonated sites were attached, the TGA displayed the corresponding loss of SO_2 at ~250 ^{o}C due to degradation of the sulfonic acid groups. The water uptake and proton conductivity of the sulfonated copolymers was investigated and the values were similar to previously studied poly(arylene ether sulfone)s prepared by direct copolymerization.[239]

8.2. Introduction

Sulfonated poly(arylene ether)s have been extensively studied as candidates for proton exchange membrane (PEM) fuel cells. In particular, post-sulfonation of poly(ether ether ketone) (PEEK) and poly(ether sulfone) (PSU) generates proton-conducting copolymers with sulfonic acid sites from commercially available materials.[240,241,242] Post sulfonation of Udel® (PSU) is generally accomplished with chlorotrimethylsilyl sulfonate, generated *in-situ* by reacting chlorosulfonic acid with

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[239] Harrison, W.L.; Wang, F.; Mecham, J.B.; Bhanu, V.A.; Hill, M.; Kim, Y.S.; McGrath, J.E. Influence of the Bisphenol Structure on the Direct Synthesis of Poly(arylene ether) Copolymers. I. *J. Polym. Sci.: Part A: Polym. Chem.* **2003**, *41*, 2264-2276.

[240] Huang, R.Y.M.; Shao, P.; Burns, C.M.; Feng, X. Sulfonation of Poly(ether ether ketone) (PEEK): Kinetic Study and Characterization. *J. Appl. Polym. Sci.* **2001**, *82*, 2651-2660.

[241] Kopitzke, R.W.; Linkous, C.A.; Anderson, H.R.; Nelson, G.L. Conductivity and Water Uptake of Aromatic-Based Proton Exchange Membrane Electrolytes. *J. Electrochem. Soc.* **2000**, *147(5)*, 1677-1681.

[242] Nolte, R.; Ledjeff, K.; Bauer, M.; Mulhaupt, R. Partially Sulfonated Poly(arylene ether sulfone) – A Versatile Proton Conducting Membrane Material for Modern Energy Conversion Technologies. *J. Membr. Sci.* **1993**, *83*, 211-220.

trimethylchlorosilane. The degree of sulfonation can be controlled by varying the reaction time and mole ratio of sulfonating agent to the polymer.[243] Due to the large amount of swelling in these membranes, the sulfonated copolymers can be intentionally or unintentionally crosslinked through the sulfonic acid groups, which results in a decrease in conductivity, swelling, and permselectivity. The reduction in conductivity is due to the loss of ion-conducting sites (sulfonic acid groups); though the membrane is still a viable material for PEMs.

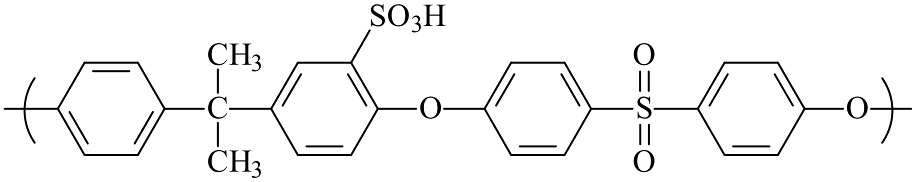

Figure 8-1. Sulfonated Udel® polysulfone generated by post-sulfonation reaction[244]

Johnson and colleagues studied the substitution position of the sulfonate group.[244] It was found that the sulfonation only occurs in the Bisphenol A aromatic ring at the activated position ortho to the ether linkage and only yields mono-substitution per repeat unit (Figure 8-1). A disadvantage of this route is that the sulfonic acid sites are on the activated ring (as opposed to the rings adjacent to the sulfone linkage) and can undergo *ipso*-substitution with H^+. Therefore, the hydrolytic stability of the sulfonated polymer might be expected to be poor under strongly acidic conditions, such as those in a fuel cell.

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[243] Lufrano, F.; Squadrito, G.; Patti, A.; Passalacqua, E. Sulfonated Poysulfone as Promising Membranes for Polymer Electrolyte Fuel Cells. *J. Appl. Polym. Sci.* **2000**, *77*, 1250-1257.

[244] Johnson, B.C.; Yilgor, I.; Tran, C.; Iqbal, M. Whightman, J.P.; Lloyd, D.R.; McGrath, J.E. Synthesis and Characterization of Sulfonated Poly(arylene ether sulfone)s. *J. Polym. Sci.: Polym. Chem. Ed.* **1984**, *22*, 721-737

In an effort to increase the hydrolytic stability of sulfonated Udel PSU, Kerres and colleagues developed a novel method to functionalize the position ortho to the sulfone group with sulfonic acid sites.[245] The electron-deficient portion of the polymer backbone was lithiated in the presence of *n*-butyllithium, and then sulfinated by adding SO_2. The corresponding sulfinate groups were converted to proton-conducting sulfonic acid sites by oxidation and acidification.

While there are several routes to post-sulfonation of poly(arylene ether sulfone)s, precision and control are lacking with these methods. Additionally, the mechanical properties of these sulfonated copolymers suffer at high ion-exchange capacities (IECs) due to the random distribution of acid sites, and perhaps, to the fact that the sulfonic acid groups are directly attached to the polymer backbone.

A different approach to prepare sulfonated PSU was introduced by Ueda in 1993.[246] Our research group modified this method to prepare wholly aromatic disulfonated poly(arylene ether sulfone)s (BPSH), and more recently fluorinated poly(arylene ether nitrile sulfone)s (6FCN) and fluorinated poly(arylene ether sulfone)s (6FSH).[239,247,248] By utilizing a disulfonated monomer, SDCDPS, the sulfonic acid

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[245] Kerres, J.; Cui, W.; Reichle, S. New Sulfonated Engineering Polymers via the Metalation Route. I. Sulfonated Poly(ether sulfone) PSU Udel® via Metalation-Sulfination-Oxidation. *J. Polym. Sci.: Part A: Polym. Chem.* **1996**, *34*, 2421-2438.

[246] Ueda, M.; Toyota, H.; Ochi, T.; Sugiyama, J.; Yonetake, K.; Mazuko, T.; Teremoto, T. Synthesis and Characterization of Aromatic Poly(ether sulfone)s Containing Pendent Sodium Sulfonate Groups. *J. Polym. Sci.: Polym. Chem. Ed.* **1993**, *31*, 853-858.

[247] Wang, F.; Hickner, M.; Kim, Y.S.; Zawodzinski, T.A.; McGrath, J.E. Direct Polymerization of Sulfonated Poly(arylene ether sulfone) Random (Statistical) Copolymers: Candidates for New Proton Exchange Membranes. *J. Membr. Sci.* **2002**, *197*, 231-242.

[248] Sumner, M.J.; Harrison, W.L.; Weyers, R.M.; Kim, Y.S.; McGrath, J.E.; Riffle, J.S.; Brink, A.; Brink, Brink, M.H. Novel Proton Conducting Sulfonated Poly(arylene ether) Copolymers Containing Aromatic Nitriles. *J. Membr. Sci.* **2004**, *239*, 199-211.

groups of the resulting copolymer are on the more stable phenyl rings adjacent to the sulfone. This direct copolymerization method leads to increased acidity of the proton-conducting sites, improved thermal and mechanical stability, precise control of the ion exchange capacity, and therefore control over the proton conductivity, water sorption and morphology of the membrane.[249]

One of the primary disadvantages of all sulfonated poly(arylene ether sulfone)s studied to date is their low proton conductivity at low relative humidity. It has been proposed by the Department of Energy and several automobile manufacturers that operation of fuel cells at high temperature (>80 °C) and low relative humidity can resolve several issues, but particularly water management. High temperature fuel cell operation also alleviates carbon monoxide poisoning of the platinum catalysts in the electrodes and improves the kinetics of the reactions. On the other hand, perfluorinated sulfonic acid membranes, such as Nafion®, display improved proton conductivity at low humidity. This inherently good proton conductivity at low humidity may be a result of the highly acidic sulfonic acid moiety and also the position of the acid. The "superacid" site is located on a side chain of the Teflon-like backbone, adjacent to an electron withdrawing $-CF_2-$ group. The flexibility of the side-chain allows for the aggregation of the sulfonic acid sites into channels, which conduct protons well. However, the proton conductivity of Nafion is reduced above 100 °C due to morphological relaxations.

Herein, the synthesis of sulfonated poly(arylene ether sulfone) copolymers where the sulfonic acid sites are on a pendent ring is reported. The properties (water sorption and proton conductivity) of sulfonated poly(arylene ether sulfone) membranes depend

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[249] Harrison, W.L.; O'Connor, K.; Arnett, N.; McGrath, J.E. Homogeneous Synthesis and Characterization of Sulfonated Poly(arylene ether sulfone)s via Chlorosulfonic Acid. *ACS Div. Polym. Chem., Polym. Preprs.* **2002**, *43,* 1159.

largely on the preparation method. Therefore we expect the properties of these pendent sulfonic acid copolymers to be different than main-chain sulfonic acid-containing copolymers.[249,250,251] By placing the acidic sites on a pendent phenyl-ether functionality, higher proton conductivities may be achieved due to aggregation of the sulfonic acids.

8.3. Experimental

8.3.1. Materials

4,4'-Dichlorodiphenylsulfone (DCDPS, Solvay Advanced Polymers) was dried at 60 ^{o}C under vacuum before use. Hydroquinone (Eastman Chemical) and methoxyhydroquinone (Aldrich) were dried at room temperature under vacuum. Potassium carbonate and barium pentafluorobenzenesulfonate were vacuum dried at 120 ^{o}C. 4-Nitrobenzenesulfonyl chloride, sodium chloride, toluene, boron tribromide, and chloroform were used as received from Aldrich. N-methyl-2-pyrrolidinone (Aldrich) and N,N-dimethylacetamide were distilled from calcium hydride under vacuum before use.

8.3.2. Monomer Synthesis: Preparation of Sodium 4-Nitrobenzenesulfonate

4-Nitrobenzenesulfonyl chloride (10 g, 45 mmol) and 20 mL of deionized water were added to a 100-mL round bottom flask equipped with a condenser and stirbar. The mixture was stirred and heated to reflux. After 4 h, the reaction was filtered to remove any insoluble impurities and cooled to room temperature. The product was "salted out"

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[250] Lufrano, F.; Gatto, I.; Staiti, P.; Antonucci, V.; Passalacqua, E. Sulfonated Polysulfone Ionomer Membranes for Fuel Cells. *Solid State Ionics* **2001**, *145,* 47-51.

[251] Kim, Y.S.; Dong, L.; Hickner, M.A.; Pivovar, B.S.; McGrath, J.E. Processing Induced Morphological Development in Hydrated Sulfonated Poly(arylene ether sulfone) Copolymer Membranes. *Polymer* **2003**, *44*, 5729-5736.

of solution by addition of sodium chloride, filtered, and dried at 120 ^{o}C under vacuum. Yield 9.85 g (97%); ^{13}C NMR (100 MHz, DMSO, d_6) δ 155 ppm (1C), 147 ppm (1C), 127 ppm (2C), 124 ppm (2C).

A practical nomenclature for the poly(arylene ether sulfone) copolymers described in this manuscript will be as follows. All of the copolymers are referred to as HQS because they are all synthesized with hydroquinone (HQ) and they are all sulfones (S). We will use the symbolism X-YY, where X refers to the pendent group [methoxy (MHQS), hydroxyl (HOHQS), benzenesulfonic acid (SHQS), tetrafluorobenzenesulfonic acid (FHQS)] and YY is the mole percent of the pendent group relative to DCDPS. For example, MHQS-40 describes the methoxy-containing poly(arylene ether sulfone) copolymer that incorporates 40 mol% of methoxyhydroquinone and 60 mol% of hydroquinone. Once this copolymer is treated with boron tribromide to convert the methoxy groups to hydroxyl substituents, the copolymer nomenclature would be HOHQS-40. If HOHQS-40 was reacted with sodium 4-nitrobenzenesulfonate, the copolymer would be called SHQS-40; and if HOHQS-40 was reacted with barium pentafluorobenzenesulfonate, the copolymer would be called FHQS-40.

8.3.3. Copolymerization of Methoxy-Containing Poly(arylene ether sulfone)s

A typical copolymerization of a methoxy-PAES with 50 mol % methoxy groups is discussed (MHQS-50). DCDPS (4.000 g, 14 mmol), hydroquinone (0.7669 g, 7 mmol), and methoxyhydroquinone (0.9760 g, 7 mmol) were introduced to a 250-mL, three neck flask equipped with a mechanical stirrer, Dean-Stark trap, condenser, and a nitrogen inlet/outlet. Potassium carbonate (2.22 g, 16 mmol) and 29 mL of NMP were added to the reaction flask to afford a 20% (w/v) solid concentration. Toluene (15 mL) was added to the flask as an azeotroping agent. The Dean-Stark trap was filled with toluene and the reaction mixture was heated to 140 ^{o}C to dehydrate the system. After 4 h at 140 ^{o}C, the Dean-Stark trap was emptied and the oil bath temperature was heated to 180 ^{o}C for 20 h. The resulting viscous solution was cooled to room temperature and precipitated into an excess of deionized water. The precipitated copolymer was collected by filtration and purified in a Soxhlet extractor with deionized water for 2 days. The resulting white, fibrous copolymer (MHQS-50) was dried under vacuum at 110 ^{o}C for at least 24 h. Yield 96%.

8.3.4. Conversion of Methoxy to Hydroxyl Groups

A typical reaction for converting MHQS-30 to HOHQS-30 is given. MHQS-30 (1.000 g) was dissolved into 20 mL of chloroform in a 100-mL, three neck flask equipped with a stirbar and nitrogen purge. BBr_3 (0.5 mL in 10 mL chloroform) was added dropwise to the reaction via a syringe. The reaction mixture was allowed to stir overnight at room temperature. The copolymer was isolated by filtration, washed with methanol (2x) and deionized water (2x), and finally dried under vacuum at 120 ^{o}C. Yield 98%.

8.3.5. Preparation of SHQS-XX Sulfonated Copolymers

HOHQS-30 (1.0000 g) and 4-nitrophenylsulfonic acid sodium salt (0.6100 g) were introduced to a 100-mL, three neck flask equipped with a mechanical stirrer, Dean-Stark trap, condenser, and a nitrogen inlet/outlet. Potassium carbonate (0.48 g) and 10 mL of DMAc were added to the reaction flask to afford a 15% (w/v) solid concentration. The reaction mixture was heated to 80 ^{o}C for 72 h. The resulting viscous solution was cooled to room temperature and precipitated into an excess of deionized water. The precipitated copolymer was collected by filtration and purified in a Soxhlet extractor with deionized water for 2 days. The resulting white, fibrous copolymer (MHQS-30) was dried under vacuum at 110 ^{o}C for at least 24 h. Yield 98 %.

8.3.6. Preparation of FHQS-XX Sulfonated Copolymers

HOHQS-30 (1.00 g) and PFBS (1.1512 g) were added to a 100-mL three-neck round bottom flask equipped with a mechanical stirrer, condenser, and a nitrogen inlet/outlet. Potassium carbonate (0.1260 g) and NMP (16 mL) were added to the reaction flask to afford a 10% (w/v) solid concentration. The reaction mixture was heated to 80 ^{o}C for 72 h. The resulting viscous solution was precipitated into 0.5M H_2SO_4, vacuum filtered, washed with deionized water (3x) and dried under vacuum at 110 ^{o}C for at least 24 h. Yield 97%.

8.3.7. Membrane Preparation and Acidification

Solutions of the copolymers were prepared by dissolving the copolymer in dimethylacetamide. The solutions were filtered and cast onto clean glass substrates. The solvent was evaporated with an infrared light for 24 hours. The sulfonate salt-form membrane was then acidified in 1.5 M sulfuric acid for 24 hours at room temperature, followed by immersion in deionized water for 24 hours at room temperature.

8.3.8. Characterization

^{1}H NMR spectra were recorded on a Varian Unity 400 instrument operating at 399.952 MHz in deuterated dimethylsulfoxide (DMSO-d_6). Infrared measurements were performed on a Nicolet Impact 400 FT-IR Spectrometer from solution cast films of polymers. Intrinsic viscosity (IV) measurements were conducted in NMP at 25 ^{o}C using a Cannon Ubbelohde viscometer. Thermo-oxidative behavior of the acid-form of the copolymers was measured on a TA Instruments TGA Q 500. Samples were dried directly in the TGA furnace at 200 ^{o}C for 2 h prior to analysis to remove water. The copolymers were evaluated from 50 ^{o}C to 800 ^{o}C in air at a heating rate of 10 ^{o}C / minute. The ion-exchange capacities (IEC) of the acid forms of the membranes were determined by nonaqueous potentiometric titration using an MCI Automatic Titrator Model GT-05. The acidified membranes were dissolved in DMAc and titrated with a standard tetramethylammonium hydroxide (TMAH) solution. The water sorption values of the sulfonated polyimide copolymers were determined at 30 ^{o}C. The membranes were vacuum-dried at 120 ^{o}C for 24 h, weighed and immersed in deionized water at room temperature for 24 h. The wet membranes were wiped dry and quickly weighed again. The water uptake of the membranes was calculated in weight percent as follows:

$$water\ uptake = [(mass_{wet} - mass_{dry}) / mass_{dry}] * 100$$

Proton conductivity measurements were performed on membranes after being soaked in deionized water for 3 days at 30 ^{o}C. An impedance spectrum was recorded from 10 MHz to 10 Hz using a Hewlett-Packard 4129A Impedance/Gain-Phase Analyzer. The cell geometry was chosen to ensure that the membrane resistance dominated the response of the system. The resistance of the membrane was taken at the frequency which produced the minimum imaginary response. All impedance measurements were performed under fully hydrated conditions. The proton conductivity was taken as the reciprocal of the resistance and reported in units of Siemens per centimeter (S/cm).

8.4. Results and Discussion

It is well known in the area of nonlinear optics (NLO) that polyimides with NLO chromophore side chains can be incorporated into the polymer chain by direct copolymerization or post-derivatization. A common synthetic route for nonlinear optical polyimides is the direct polymerization of dianhydrides with diamines containing an NLO chromophore via a poly(amic acid) prepolymer.[252] This method, however, often involves a tedious synthesis of the chromophore-containing diamine monomers. Sometimes, the fact that few chromophores can survive the relatively harsh chemical conditions of the monomer synthesis limits the kind of chromophores that are incorporated in the polyimide backbone.[253] To avoid the synthesis of chromophore-containing diamine compounds, an alternate synthetic route was devoped by Chen *et al.*[254] A one-pot preparation of a preimidized, hydroxyl-containing polyimide was developed, followed by the covalent attachment of a chromophore to the backbone of the polyimide.

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[252] Yang, S.; Peng, Z.; Yu, L. Functionalized Polyimides Exhibiting Large and Stable Second-Order Optical Nonlinearity. *Macromolecules* **1994**, *27*, 5858-5862.

[253] Chen, T.-A.; Jen, A.K.-Y.; Cai, Y. Facile Approach to Nonlinear Optical Side-Chain Aromatic Polyimides with Large Second-Order Nonlinearity and Thermal Stability. *J. Am. Chem. Soc.* **1995**, *117*, 7295-7299.

[254] Chen, T.-A.; Jen, A.K.-Y.; Cai, Y. Two-Step Synthesis of Side-Chain Aromatic Polyimides for Second-Order Nonlinear Optics. *Macromolecules* **1996**, *29*, 535-539.

This post-derivatization method may also have an application in the synthesis of proton exchange membranes for fuel cells. Instead of bonding the NLO chromophore to the polymer backbone, ion-conducting sites could be introduced. Unfortunately, the hydrolytic stablility of sulfonated polyimides under fuel cell conditions is unsatisfactory. On the other hand, poly(arylene ether sulfone)s are good film-forming materials with high thermal stability, good oxidative and hydrolytic stability, and have largely been researched as candidates for PEMs.

Hydroxyl-containing poly(arylene ether sulfone)s cannot be prepared directly due to the high reactivity of phenolic groups in the nucleophilic aromatic substitution reaction, which would result in highly branched polymers. Therefore, the copolymers must be prepared in the protected methoxy form, followed by conversion to the reactive hydroxyl form in a post-polymerization reaction.

Poly(arylene ether sulfone) copolymers with pendent methoxy groups were synthesized by nucleophilic substitution of 4,4'-dichlorodiphenylsulfone, hydroquinone, and methoxyhydroquinone (Figure 8-2). The methoxy groups are not reactive under nucleophilic aromatic substitution conditions, so high molecular weight linear polymers were obtained. The molar ratio of methoxyhydroquinone to hydroquinone was changed to produce a systematic series of poly(arylene ether sulfone) copolymers with varying amounts of methoxy groups. Potassium carbonate was selected as the weak base since it has been previously shown to facilitate the substitution reaction while minimizing side reactions. In addition, potassium carbonate has limited reactivity towards aryl halides at low temperatures, allowing the complete generation of the bis-phenate before the temperature is increased to initiate substitution. High molecular weight copolymers were synthesized in N-methylpyrrolidinone at 180 °C and characterized by intrinsic viscosity (Table 8-1) and ^{1}H NMR (Figure 8-3). The incorporation of the methoxyhydroquinone was found to be quantitative through integration of the peak at 3.6 ppm with respect to one in the aromatic region (7.9 ppm) (Table 8-1).

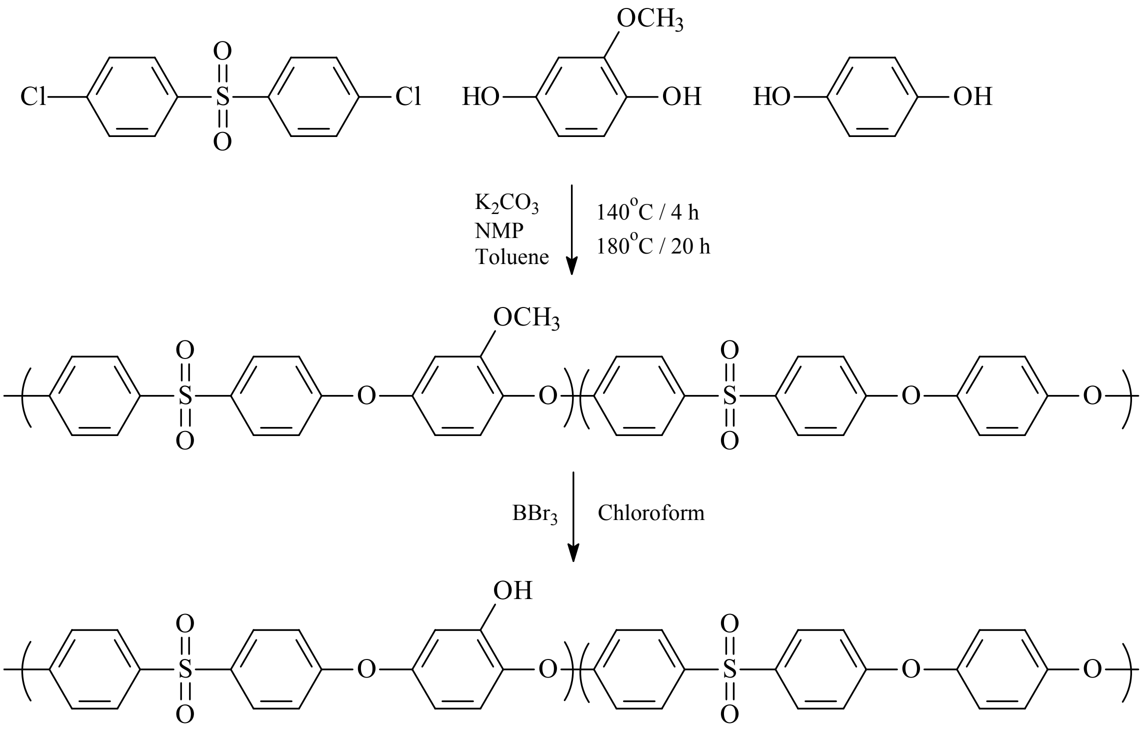


Figure 8-2. Direct synthesis of methoxy-containing poly(arylene ether sulfone)s and conversion to hydroxyl-containing copolymers

Table 8-1. Selected properties of MHQS-XX copolymers

Copolymer Composition	IV (dL/g)	% Methoxy Groups via ^{1}H NMR	5% Weight Loss Temperature (^{o}C)*	Char Yield (%)*	T_g (^{o}C)
10	0.80	8	408	2.5	202
20	0.83	18	410	2.2	298
30	0.83	30	406	2.5	195
40	0.81	39	408	2.1	195
50	0.84	46	408	2.9	200

*TGA samples were heated at 10 ^{o}C / min. in air.

All of the MHQS-XX copolymers were soluble in chlorinated solvents; therefore the conversion of the methoxy groups to reactive hydroxyl groups using BBr_3 was conducted in chloroform. Due to the polar nature of the hydroxyl groups, the subsequent HOHQS-XX copolymers were not soluble in chloroform allowing for straightforward isolation. The intrinsic viscosity of the HOHQS-XX copolymers was higher than the MHQS-XX copolymers in all cases (Table 8-2). This effect is possibly due to hydrogen bonding of the hydroxyl groups. The quantitative conversion of methoxy groups to hydroxyl groups was determined by ^1H NMR (Figure 8-3). The complete disappearance of the protons of the methoxy group (3.6 ppm) and appearance of a peak at ~10 ppm (due to –OH) was observed for all the copolymers. Additionally, an increase in the glass transition temperatures of the HOHQS-XX copolymers with respect to the MHQS-XX copolymers can be attributed to hydrogen bonding which decreases chain mobility (Figure 8-4). The T_g also increased as more hydroxyl groups were introduced to the polymer backbone (Table 8-2). The thermal stability of the MHQS-XX and HOHQS-XX copolymers were analyzed by thermogravimetric analysis in air (Figures 8-5 and 8-6). Both series of copolymers showed similar TGA profiles (5% weight loss temperatures and char yield) indicating that the methoxy and hydroxyl substituents did not influence the thermal stability.

Table 8-2. Selected properties of HOHQS-XX copolymers

Copolymer Composition	IV (dL/g)	% Methoxy Groups via ^{1}H NMR	5% Weight Loss Temperature (^{o}C)*	Char Yield (%)*	T_g (^{o}C)
10	1.05	8	402	0.22	205
20	1.00	21	400	0.57	208
30	1.09	27	409	0.95	211
40	1.02	38	399	0.43	216
50	1.30	45	404	0.01	218

*TGA samples were heated at 10 ^{o}C / min. in air.

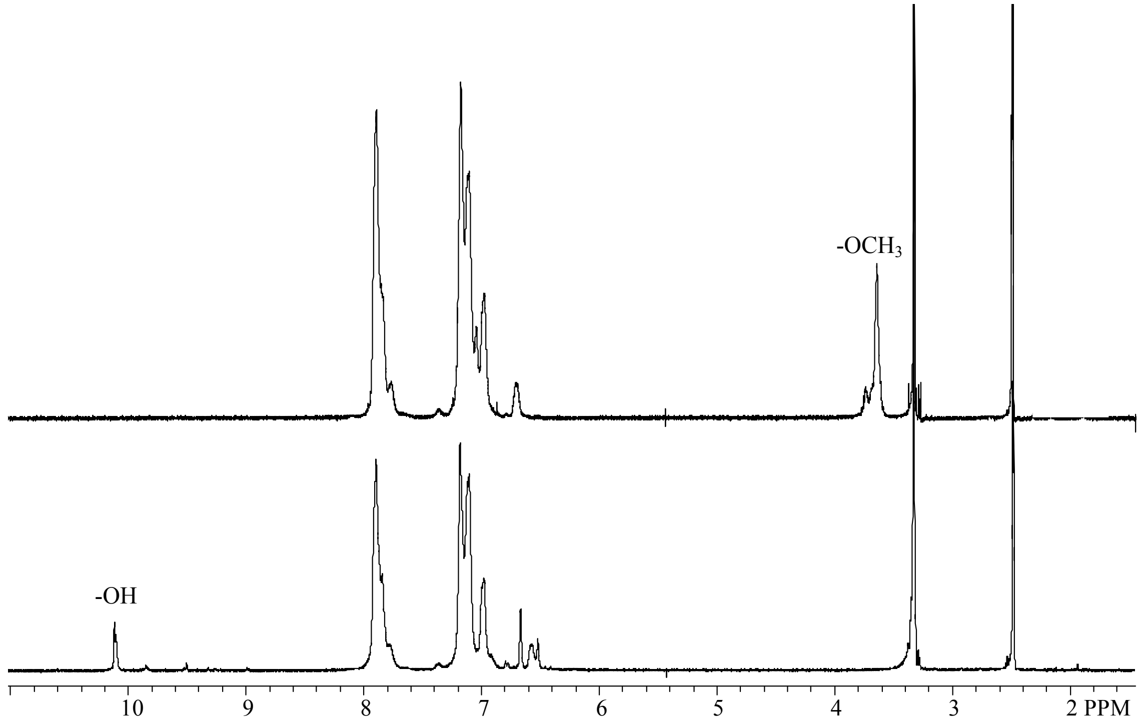


Figure 8-3. ^{1}H NMR of MHQS-40 (top) and HOHQS-40 (bottom)

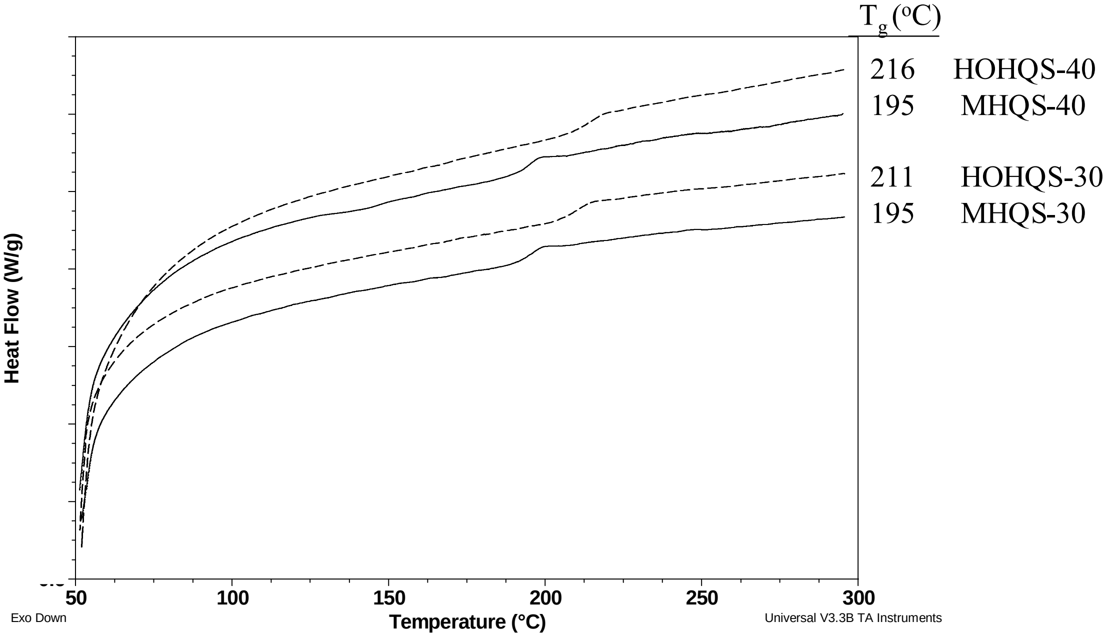


Figure 8-4. Representative DSC curves of methoxy- and hydroxyl-containing copolymers

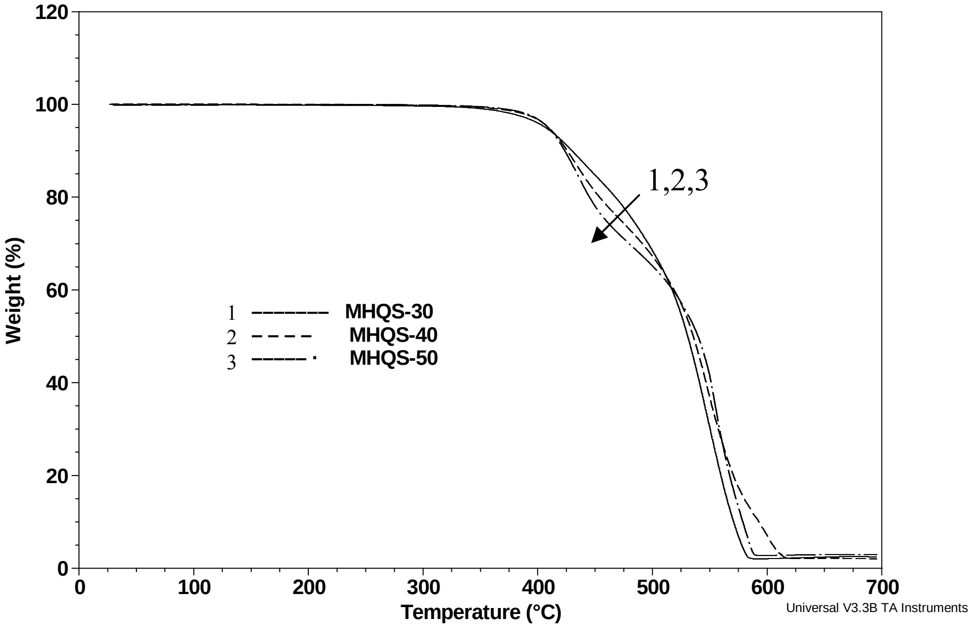


Figure 8-5. TGA plot of methoxy-containing poly(arylene ether sulfone) copolymers

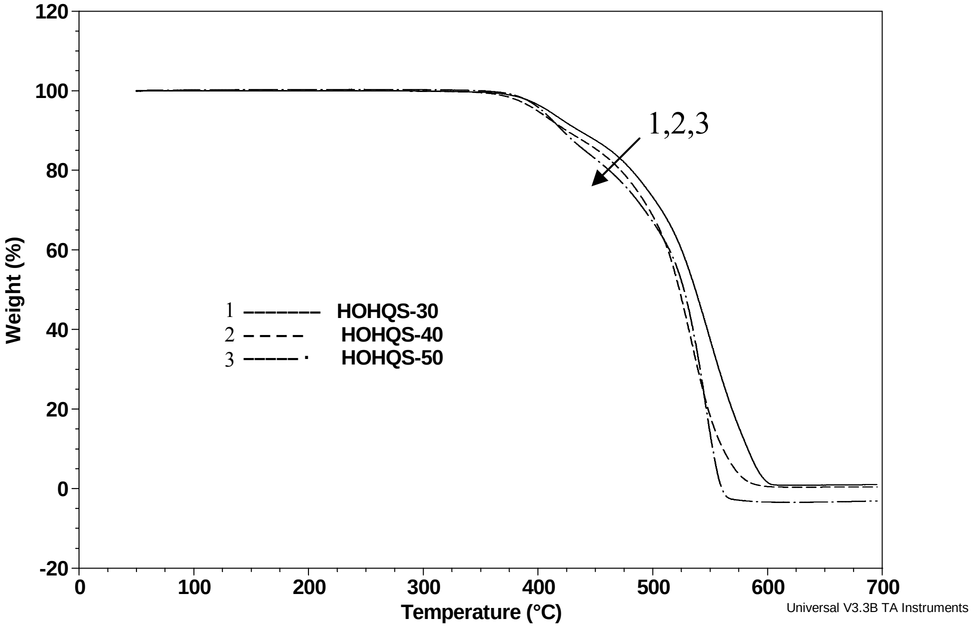


Figure 8-6. TGA plot of hydroxyl-containing poly(arylene ether sulfone) copolymers

The hydroxyl-containing copolymers were reacted under nucleophilic conditions with either sodium 4-nitrobenzenesulfonate (SHQS-XX) or barium pentafluorobenzenesulfonate (FHQS-XX) to prepare sulfonated copolymers (Figures 8-7 and 8-8). The derivatization reactions were only heated to 80 ^{o}C to minimize the ether-ether interchange reactions that could possibly occur. Additionally, in the case of the reactions of barium pentafluorobenzenesulfonate with HOHQS, low temperature was needed to provide materials that did not crosslink. Highly fluorinated monomers are very reactive, so typically reaction temperatures are kept below 100 ^{o}C. With these two series of copolymers (SHQS-XX and FHQS-XX), we hoped to establish how the acidity of the sulfonic acid group influences the PEMs properties, i.e. water uptake and proton conductivity. Both series of sulfonated copolymers were prepared with ion-exchange capacities ranging from 0.3 to 0.8 meq/g.

The incorporation of sodium 4-nitrobenzenesulfonate was quantitative as shown by the additional ^{1}H NMR peaks at 7.85 ppm and 8.4 ppm, with respect to the parent polymer (Figure 7-7). Since barium pentafluorobenzenesulfonate has no hydrogens that could be monitored via ^{1}H NMR, the disappearance of the hydroxyl peak at 10 ppm and the shift of the protons on the adjacent benzene ring clearly showed that the reaction proceeded as expected (Figure 8-9). Additionally, the FT-IR displayed additional absorbances at 1030 cm^{-1} and 1098 cm^{-1} corresponding to the symmetric and asymmetric stretching of sulfonic acid groups. The TGA profile also showed the characteristic drop ~250 ^{o}C due to the loss of sulfonic acid groups (Figure 8-10).

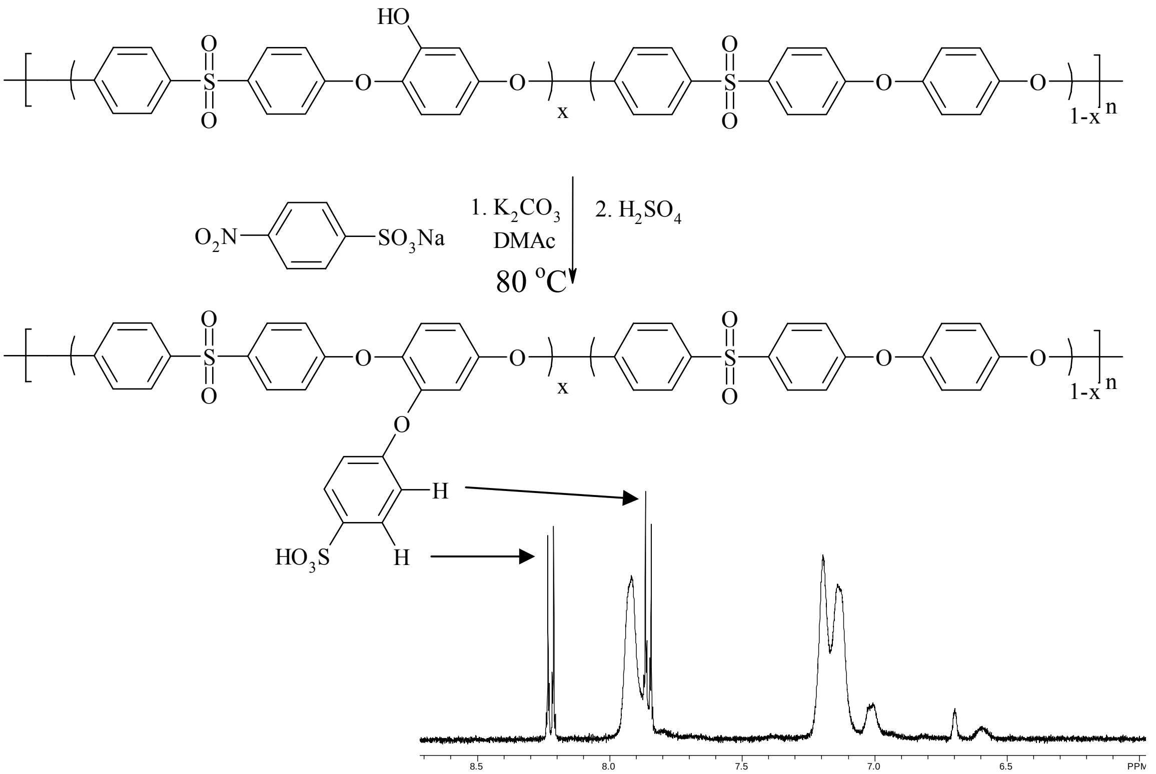


Figure 8-7. Synthesis of sulfonated poly(arylene ether sulfone) copolymers (SHQS-XX) and ^{1}H NMR of SHQS-30.

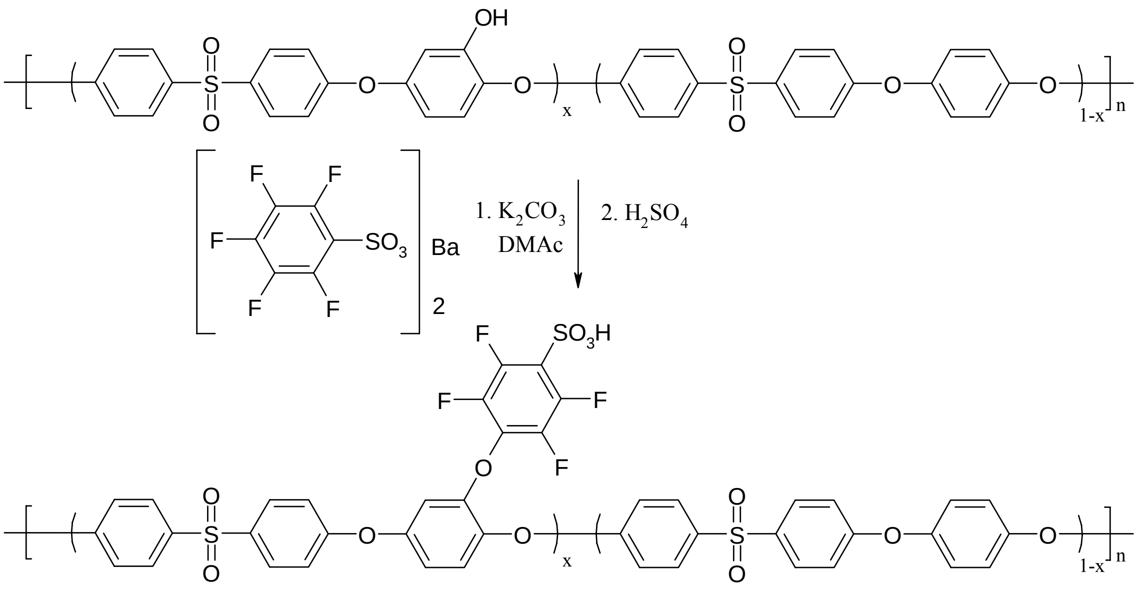


Figure 8-8. Synthesis of fluorine-containing sulfonated poly(arylene ether sulfone)s (FHQS-XX)

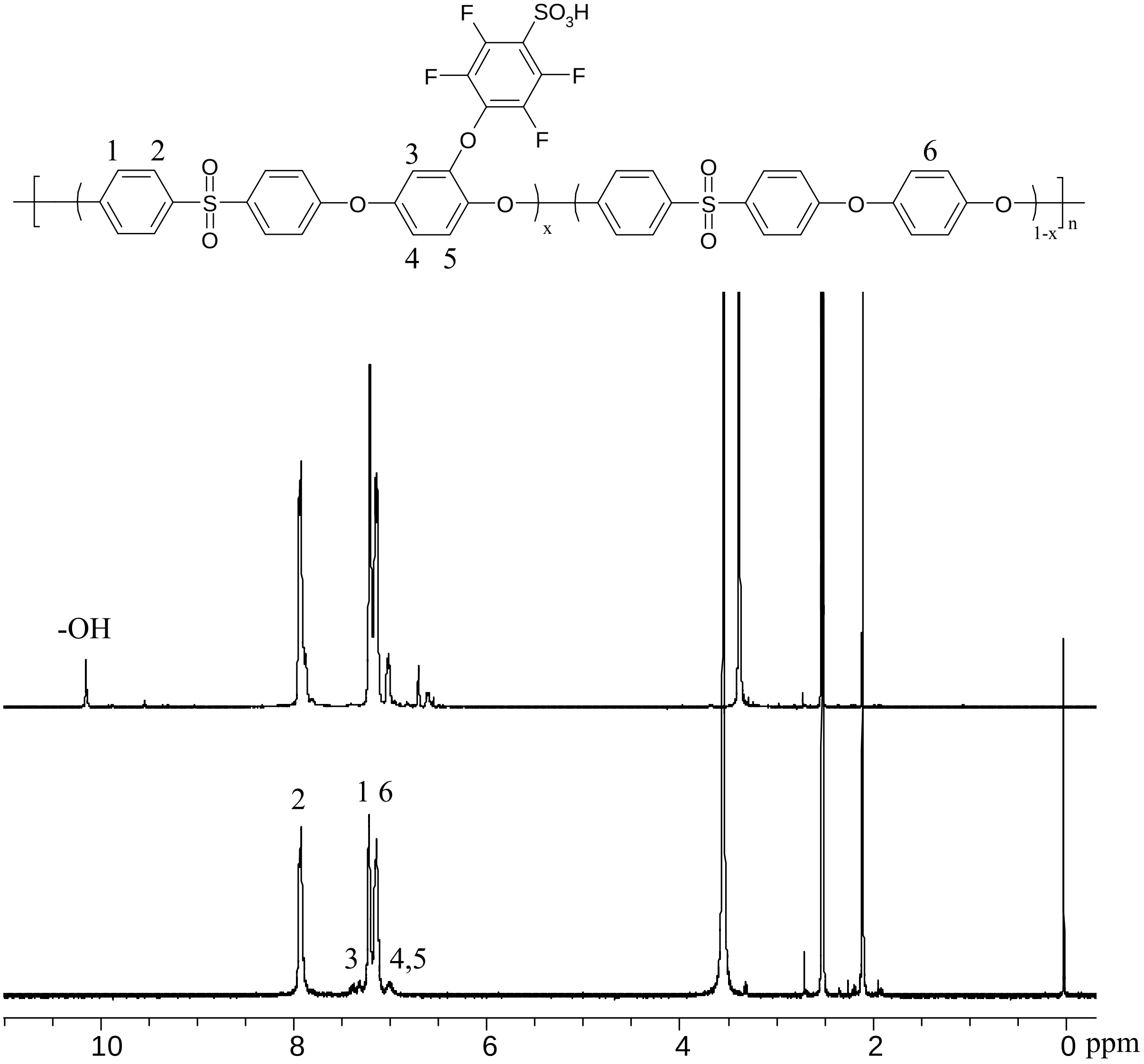


Figure 8-9. ^{1}H NMR of HOHQS-30 (top) and FHQS-30 (bottom).

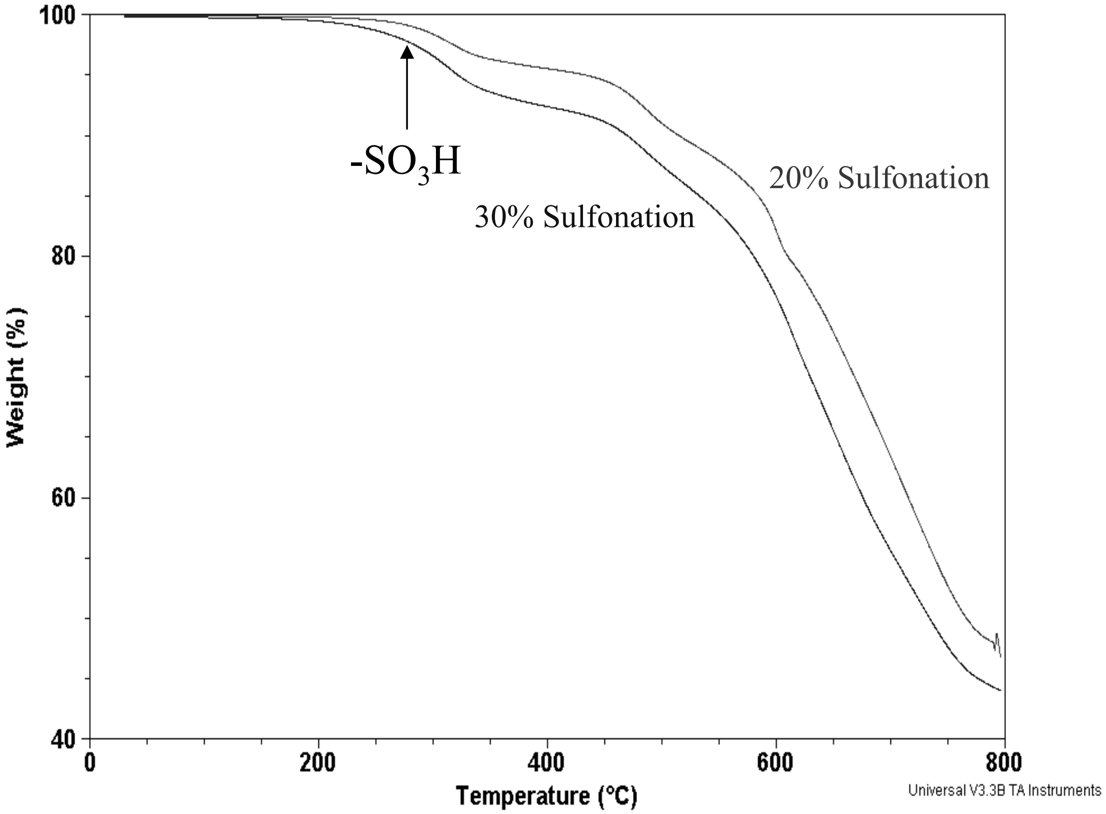
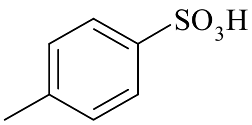
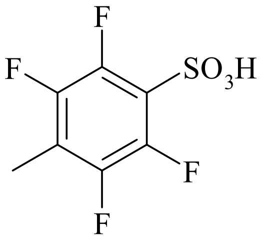


Figure 8-10. TGA profile of FHQS-20 (top) and FHQS-30 (bottom) (10 °C/min. in air).

The high molecular weight sulfonated copolymers formed clear transparent, tough, ductile membranes when solution cast from N,N-dimethylacetamide. The water sorption and proton conductivities of the copolymers were determined after soaking the membranes in deionized water at 30 °C for 48 hours (Table 8-3). The proton conductivities of both series of copolymers were fairly low (1-8 mS/cm), particularly when compared to Nafion (100 mS/cm). However, the water uptake and proton conductivity values are similar to previously studied poly(arylene ether sulfone)s prepared by direct copolymerization at equivalent ion exchange capacities.

Table 8-3. Selected properties of sulfonated poly(arylene ether sulfone) copolymers

Copolymer	Ion Exchange Capacity (meq/g)		Water Sorption (%)	Proton Conductivity* (S/cm)
	Calculated	Experimental		
	0.29	0.3	6	0.001
	0.56	0.5	15	0.005
	0.80	0.9	20	0.008
	0.29	0.2	8	0.002
	0.54	0.5	12	0.004
	0.75	0.7	18	0.008

8.5. Conclusions

High molecular weight, film-forming sulfonated poly(arylene ether sulfone) copolymers were prepared in three steps; copolymerization, deprotection, and functionalization. The reactions were monitored via IV, NMR, FT-IR, TGA, and DSC. The sulfonic acid-functionalized copolymers displayed low proton conductivities, probably due to the low ion exchange capacities of the materials. Efforts are ongoing to generate similar materials with higher ion exchange capacities to improve the proton conductivity. Highly sulfonated copolymers could not be synthesized herein due to the low solubility of the copolymers as more hydroxyl groups were introduced. Additionally, it was difficult to distinguish how the fluorine groups (SHQS-XX vs. FHQS-XX) influenced the copolymer properties due to the fact that the levels of sulfonation were so low.

8.6. Acknowledgements

The authors would like to thank the Department of Energy (DE-FC36-01G01086) for support of this research effort.

CHAPTER 9

CONCLUSIONS

The primary objectives of this research were to systematically synthesize series of sulfonated high temperature copolymers and to characterize them as potential proton exchange membranes (PEMs) by investigating their film-forming characteristics, ion exchange capacity, thermal and hydrolytic stability, water sorption, and proton conductivity. Heterocyclic polymers are currently applied in many high performance areas such as microelectronics, automotive, gas separation and aerospace due to their excellent thermal and mechanical properties. These properties, along with the ability to form tough, ductile films, suggested that they might be good candidates for PEMs.

Three series of disulfonated, low strain six-membered ring polyimide copolymers were synthesized from a novel disulfonated diamine (3,3'-disulfonic acid-bis[4-(3-aminophenoxy)phenyl]sulfone, SA-DADPS), three nonsulfonated diamines and 1,4,5,8-naphthalenetetracarboxylic dianhydride. SA-DADPS was synthesized to improve the water stability of the resulting six-membered ring copolyimides. The synthesis of this diamine proved to be more difficult than its nonsulfonated counterpart. However, SA-DADPS was successfully synthesized in high yield in NaOH/DMAc and easily purified by recrystallization in deionized water. The series of disulfonated polyimide copolymers varying in IEC derived from SA-DADPS provided improved solubility, ductility, and hydrolytic stability compared to the more rigid 4,4'-diamino-2,2'-biphenyl disulfonic acid (BDA)-type polyimides. The influence of copolymer composition and ion exchange capacity on water sorption, proton conductivity and water stability at 80 °C was studied. The structure of the nonsulfonated diamine largely influenced the copolymer stability in water at 80 °C, but it had little effect on the proton conductivity and water sorption at comparable IECs. Additionally, the initial DMFC performance of these membranes was exceptional. Although the polyimides had relatively low proton conductivities, the methanol crossover of the membranes was much lower than Nafion or disulfonated poly(arylene ether sulfone)s. While these polyimides may not be useful materials for fuel cells at 80 °C because of their inherently low hydrolytic stability, they have allowed us to gain insight into the necessary properties for a successful DMFC membrane.

Due to the poor hydrolytic stability of the polyimides, other heterocyclic polymers, such as sulfonated polybenzoxazoles and polybenzimidazoles, were investigated. A novel disulfonated diacid, SODBA, was prepared to enhance the solubility of the diacid in poly(phosphoric acid), which may be used to synthesized higher molecular weight materials. A series of partially fluorinated disulfonated polybenzoxazoles with controlled degrees of disulfonation were prepared by varying the stoichiometric ratio of sulfonated diacid (SODBA) to the nonsulfonated diacid (ODBA). The water uptake and proton conductivity of the membranes increased with the degree of sulfonation; but both were far lower than comparable poly(arylene ether) systems. The hydrogen/air fuel cell performance was tested with the 100% disulfonated PBO membrane. Although the performance was an improvement over Nafion 117 under the same conditions, the membrane became brittle during testing. The instability of the polybenzoxazoles was attributed to the partial positive charge on the carbon of the heterocyclic ring. The hydrolytic stability of the membranes was improved by the incorporation of electron-donating ether linkages, nevertheless the sulfonated copolymers quickly became brittle after boiling in deionized water for even one hour.

A series of novel disulfonated poly(arylene ether benzimidazole)s was synthesized via nucleophilic aromatic polycondensation of disodium-3,3’-disulfonate-4,4’-dichlorodiphenylsulfone (S-DCDPS), 4,4’-dichlorodiphenylsulfone and a benzimidazole bisphenol (HPBI). The hydrolytically stable copolymers displayed inherently high intrinsic viscosities, due in part to their high molecular weights, but also because of the intermolecular association of the sulfonate sites with the basic imidazole groups. The disulfonated polybenzimidazole membranes exhibited lower water uptake and proton conductivity compared to similar poly(arylene ether)s. Additionally, the thermal degradation of the sulfonate salt and sulfonic acid membranes was similar, suggesting an interaction between the sulfonic acid groups and the imidazole rings. The excellent thermal and hydrolytic stability of the benzimidazole groups justifies further investigation.

The influence of benzimidazole moieties on disulfonated poly(arylene ether sulfone) copolymers was studied. The addition of benzimidazole groups into random copolymers was accomplished by incorporating a benzimidazole bisphenol in the copolymerization step. Membranes were also prepared by blending (poly(5,5’-benzimidazole-2,2’-diyl-1,3-phenylene) (PBI) and highly disulfonated poly(arylene ether sulfone) copolymers. In both the random copolymer and the 6FSH-60/PBI blend membranes, the introduction of benzimidazole concentrations decreased the water uptake and proton conductivity of the membranes in water at 30 ^{o}C. It was found that the smallest addition of benzimidazole (< 5%) provided for the best selectivity, i.e. lowest drop in proton conductivity but highest decrease in water uptake.

It has been proposed that the aggregation of side-chain sulfonic acid sites to form ion channels enhances the proton conductivity of Nafion membranes. A series of side-chain sulfonated poly(arylene ether sulfone) copolymers was synthesized in order to combine this advantage with the stability of poly(arylene ether)s. Methoxy-containing copolymers were prepared via direct copolymerization to control the ion exchange capacity of the resulting PEMs. The methoxy groups were deprotected to afford reactive phenolic sites. Nucleophilic aromatic substitution reactions were used to prepare optionally fluorinated aryl sulfonated copolymers. The proton conductivity and water sorption of the resulting copolymers increased with the ion exchange capacity but showed no trend with acidity.

The investigation of high temperature polymers for fuel cell applications, as discussed in the preceding chapters, has allowed us to gain valuable insight into the properties necessary for a successful PEM.

CHAPTER 10

SUGGESTED FUTURE RESEARCH

The results outlined in the previous chapters have demonstrated the properties of several series of random copolymers for proton exchange membrane fuel cells. Unfortunately all of these copolymer systems suffer from high water sorption values at high proton conductivities. In random copolymers, the connectivity of the hydrophilic phase at high ion exchange capacities results in membranes with very high water swelling and therefore low mechanical properties. One way to alleviate this problem is to develop graft or block copolymers. Graft copolymers of polystyrene-*g*-polystyrenesulfonate displayed lower water uptakes and higher proton conductivities compared to random polystyrene/polystyrenesulfonate copolymers.[255] This result is actually a two-fold improvement because it has also been suggested that the lifetime of a fuel cell can be enhanced by preparing membranes with similar swelling to the attached electrodes.[256] Typically, this means lower water uptakes when using Nafion-based electrodes. However, the stability of sulfonated polystyrene under the aggressive conditions of a fuel cell is not satisfactory. This immediately suggests the use of poly(arylene ether)s with appropriate ion-conducting sites, due to their excellent, thermal, chemical and oxidative stability. Under the nucleophilic conditions of poly(arylene ether) synthesis, the polymer

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[255] Ding, J.; Chuy, C.; Holdcroft, S. Enhanced Conductivity in Morphologically Controlled Proton Exchange Membranes: Synthesis of Macromonomers by SFRP and Their Incorporation into Graft Copolymers. *Macromolecules* **2002**, *35*, 1348-1355.

[256] Kim, Y.S.; McGrath, J.; Pivovar, B. The Importance of Interfaces in Membrane Optimization for DMFCs. *Abstracts of the 206th Electrochemical Society Meeting* **2004**, *2004-02*, 1471.

undergoes ether-ether interchange reactions that randomize the chains. This effect makes it difficult to prepare wholly poly(arylene ether) block or graft copolymers.

A suggestion for future research would be to synthesize block and graft copolymers with six-membered ring imide linkages. Although the random disulfonated polyimide membranes became brittle in water at 80 ^{o}C, the homopolymer of *m*-BAPS and NDA displayed no hydrolytic degradation. In the case of block or graft copolymers, this suggests that as long as the hydrophilic domain, composed of disulfonated poly(arylene ether), was sufficiently separated from the hydrophobic polyimide chains, degradation may not occur. As for the preparation of graft copolymers, disulfonated poly(arylene ether) oligomers could be reacted with a nonsulfonated six-membered ring polyimide bearing reactive hydroxyl groups along the backbone. The hydroxyl-containing polyimide could be prepared by reacting a bis(*o*-aminophenol), such as 2,2'-bis(3-amino-4-hydroxyphenyl)-hexafluoropropane (6FAP) (Chapter 5), and 1,4,5,8-naphthalenetetracarboxylic dianhydride in *m*-cresol. This polyimide would then be directly added to the direct polymerization of a highly sulfonated poly(arylene ether). As for block copolymers, amine-terminated disulfonated poly(arylene ether) oligomers could be synthesized and isolated. Once characterized, these oligomers would be added directly to a polyimide polymerization to prepare completely alternating hydrophilic-poly(arylene ether)/hydrophobic-polyimide copolymers. The hydrophilic amine-terminated poly(arylene ether) could also be reacted with an anhydride-terminated poly(arylene ether) to synthesize perfectly alternating multiblock poly(arylene ether) copolymers.

CHAPTER 11

VITA of Brian Russel Einsla

Brian Russel Einsla, son of Wheeler and Patricia Einsla, was born on January 29, 1978 in Wilkes-Barre, Pennsylvania. He is the older brother to Christopher Einsla, and the grandson of Russel and Marie Einsla, and Raymond and Mary Clarke. Brian was raised in Chalfont, Pennsylvania and graduated from Central Bucks West High School in 1996. In August of the same year, he started his undergraduate studies at Virginia Polytechnic Institute and State University, where he also worked part-time as a laboratory technician under Dr. James E. McGrath. During school breaks, Brian worked at Penn Color, Inc in Hatfield, PA. In May 2000, he graduated from Virginia Tech with a B.S. in Chemistry. In the spring of 2001, he began his graduate career in the Ph.D. program at Virginia Tech under the advisement of James E. McGrath. Brian spent the summer of 2003 as a visiting researcher at Los Alamos National Laboratories in the Electronic and Electrochemical Materials and Devices division. Upon completion of his Ph.D. degree in Macromolecular Science and Engineering in May 2005, the author will join Henkel as a Senior Development Chemist in the Fuel Cell Team at Rocky Hill, Connecticut.